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## PROCEEDINGS

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#### PROCEEDINGS OF

### THE ROYAL SOCIETY.

SECTION A.—MATHEMATICAL AND PHYSICAL SCIENCES.

The Kinetic Theory of Simple and Composite Monatomic Gases: Viscosity, Thermal Conduction, and Diffusion.

By S. Chapman, M.A., D.Sc., Fellow and Lecturer of Trinity College, Cambridge.

(Communicated by Sir J. Larmor, F.R.S.)

(Abstract.\*)

#### INTRODUCTION.

The mean-free-path phenomena of gases can be explained in a general way by a very elementary form of the kinetic theory, but to develop a satisfactory mathematical treatment of them, yielding accurate numerical results, is less easy. The difficulty varies to some extent with the nature of the molecular model chosen as basis. It is curious that the adoption of one particular model, viz., a centre of force varying inversely as the fifth power of the distance, removes nearly all the analytical complications in the theory. The first accurate treatment of viscosity, conduction, and diffusion, due to Maxwell, was made possible by this fact, and it is remarkable that Maxwell's theory requires no knowledge of the velocity-distribution function corresponding to the non-uniform state of the gas. If the molecules are of any

\* This abstract summarises two papers in the 'Philosophical Transactions,' the first (received October 5, 1915) dealing with simple gases ('Phil. Trans.,' A, vol. 216, pp. 279-348, 1915), and the second (received May 19, 1916) with composite gases. These two papers amplify and complete an earlier memoir ('Phil. Trans.,' A, vol. 211, pp. 433-483 (1911)), which contains a first approximation to the present theory.

other type, the function must be determined, a task wherein lies the main difficulty of the investigation. It is, however, of more than mathematical interest to widen the basis of the theory, since Maxwell's molecular model does not satisfactorily represent the molecules of actual gases.

The velocity-distribution function has been proved by Boltzmann to satisfy a certain integral equation, which Hilbert has shown to be sufficient to determine the function uniquely. Lorentz has solved an important degenerate form of this equation, while Pidduck\* has obtained solutions of some typical examples of the general case, and so deduced many interesting numerical results relating to diffusion. The present method, however, is not based on Boltzmann's equation. Though less direct, it seems to possess advantages not shared by the other method, in that it yields results of complete formal generality, which can be reduced to numerical form with comparatively little arithmetical labour. To comply with the requirements of the pure mathematician, the results should be proved to be in conformity with Boltzmann's equation. Progress has already been made in this direction, and has brought to light several theorems of much analytical interest. As the insertion of these would be unsuitable in memoirs intended primarily to deal with questions of physics, they are reserved for a future paper.

#### PART I .- OUTLINE OF THE MATHEMATICAL METHOD.

#### (1) Notation and Analysis of the State of the Gas.

We consider a gas composed of a mixture of two sets of spherically symmetrical molecules of masses  $m_1$ ,  $m_2$ ,† in numbers  $\nu_1$ ,  $\nu_2$  per unit volume at (x, y, z, t).‡ The component densities  $\rho_1$ ,  $\rho_2$ , are consequently equal to  $\nu_1 m_1$ ,  $\nu_2 m_2$ . The external force acting on each molecule  $m_1$  (and similarly for the molecules  $m_2$ , with change of suffix throughout) will be denoted by  $(X_1, Y_1, Z_1)$ , or, vectorially, by P, while the mean velocity of this group of molecules at (x, y, z, t) will be denoted by  $(u_1, v_1, w_1)$  or vectorially by  $c_1$ . The proportions of either kind of gas will be denoted by  $\lambda_1$ ,  $\lambda_2$ , so that

$$\lambda_1 = \nu_1/\nu_0, \quad \lambda_2 = \nu_2/\nu_0,$$

$$= \nu_1 + \nu_0 \quad \text{evidently } \lambda_1 + \lambda_2 = 1$$

where

$$\nu_0 = \nu_1 + \nu_2$$
; evidently  $\lambda_1 + \lambda_2 = 1$ .

<sup>\*</sup> Boltzmann, 'Vorlesungen über Gastheorie,' vol. 1, p. 114; Hilbert, 'Math. Ann. (1912); Lorentz, 'Theory of Electrons,' p. 268; Pidduck, 'Proc. Lond. Math. Soc., (2), vol. 15, p. 89 (1915). Also of. Lunn, 'Bull. Amer. Math. Soc.,' vol. 19, p. 455 (1913); Enskog, 'Phys. Zeit.,' vol. 12, p. 58 (1911).

<sup>†</sup> For convenience we shall suppose the heavier gas to be taken as gas (1), so that  $m_1 > m_2$ .

<sup>‡</sup> I.e., at the point (x, y, z), and at time t.

The suffix 0 here, and throughout, refers to the composite gas as a whole. Thus the mean mass  $m_0$ , or external force  $P_0$  (or  $X_0$ ,  $Y_0$ ,  $Z_0$ ) per molecule, and the mean velocity  $c_0$  (or  $u_0$ ,  $v_0$ ,  $w_0$ ) of the gas as a whole, are given by equations of the type

$$m_0 = \lambda_1 m_1 + \lambda_2 m_2, \qquad X_0 = \lambda_1 X_1 + \lambda_2 X_2.$$

and so on. Evidently, the total density  $\rho_0$ , equal to  $\rho_1 + \rho_2$ , is also given by  $\nu_0 m_0$ . The suffix 0, together with a dash ('), will relate to certain multiples of the difference between the values of various data for the component gases.

Thus we define  $\lambda_{\theta}'$ ,  $m_{\theta}'$ ,  $\rho_{\theta}'$ ,  $P_{\theta}'$ ,  $c_{\theta}'$  by the equations

$$2\lambda_0' = \lambda_1 - \lambda_2, \quad m_0' = \lambda_1 \lambda_2 (m_1 - m_2), \quad \rho_0' = \nu_0 m_0' / \lambda_1 \lambda_2 = \nu_0 (m_1 - m_2),$$

$$P_0' = \lambda_1 \lambda_2 (m_2 P_1 / m_0 - m_1 P_2 / m_0), \quad c_0' = \lambda_1 \lambda_2 (c_1 - c_2).$$

By inverting the above equations, we obtain the following expressions for the original quantities  $m_1$ ,  $P_1$ , etc., in terms of  $m_0$ ,  $m_0'$ ,  $P_0$ , and so on:—

$$m_1 = m_0 + m_0'/\lambda_1$$
,  $P_1 = m_1 P_0/m_0 + P_0'/\lambda_1$ ,  $c_1 = c_0 + c_0'/\lambda_1$ ,  
 $m_2 = m_0 - m_0'/\lambda_1$ ,  $P_2 = m_2 P_0/m_0 - P_0'/\lambda_2$ ,  $c_2 = c_0 - c_0'/\lambda_2$ ,

It may readily be seen that the motion of the gas can be analysed into (a) a steady motion of the gas as a whole with velocity  $c_0$ , together with (b) a motion of interdiffusion in which equal numbers  $(\nu_0c_0)$  per second) of the two groups of molecules are transported in opposite directions, the mean velocities of the two streams being  $c_0'/\lambda_1$  and  $-c_0'/\lambda_2$ . The momentum of the common motion (a) is  $\rho_0c_0$ , while the resultant momentum of the motion of interdiffusion (due to the difference of molecular mass) is  $\rho_0'c_0'$ ; it is easily seen that, with the above definitions,

$$\rho_1 c_1 + \rho_2 c_2 = \rho_0 c_0 + \rho_0' c_0'.$$

As regards the resolution of the forces into multiples of  $P_0$  and  $P_0'$ , the first terms,  $m_1P_0/m_0$  on  $m_1$  and  $m_2P_0/m_0$  on  $m_2$ , represent forces which will impart a common acceleration  $P_0/m_0$  to each group of molecules (we may suppose this to modify the common stream-velocity  $c_0$ ). The remaining components of  $P_1$  and  $P_2$ , when summed up over the  $\nu_1$  or  $\nu_2$  molecules of the corresponding group, afford equal and opposite total forces  $\pm \nu_0 P_0'$ ; such interdiffusing groups of molecules as we consider in (b) will exert equal and opposite forces on one another, and the forces acting on the two groups must be equal and opposite if the motion of interdiffusion is to be maintained, or modified without imparting any common velocity to them. As for  $\lambda_0'$ , it is introduced for the sake of symmetry: D denoting any differential operator, clearly

$$D\lambda_1 = -D\lambda_2 = \frac{1}{2}D(\lambda_1 - \lambda_2) = D\lambda_0'$$

We next consider the motions of individual molecules. The velocity of a typical molecule  $m_1$  will be denoted by  $(u)_1$ ,  $(v)_1$ ,  $(w)_1$ , or  $(c)_1$ , when referred to the co-ordinate axes, or when referred to axes moving with the velocity  $c_0$  appropriate to the given values of (x, y, z, t), by  $U_1$ ,  $V_1$ ,  $W_1$  or  $C_1$ . Thus,

$$C_1 = (c)_1 - c_0, C_2 = (c)_2 - c_0,$$

the second equation referring to the molecules  $m_2$ .

The mean value of any function of the molecular velocities will be denoted by a bar placed above the expression for the function. Hence, by definition,

$$\overline{(c)_1} = c_0 + \overline{C_1} = c_1,$$
  $\overline{(c)_2} = c_0 + \overline{C_2} = c_2,$ 

or

$$\overline{C_1} = c_1 - c_0 = c_0'/\lambda_1, \qquad \overline{C_2} = c_2 - c_0 = -c_0'/\lambda_2.$$

So far, C has denoted a vector quantity, and the equations involving it have been vectorial: henceforward it will denote the amplitude of the vector, so that C is essentially positive, and

$$C_1^2 = U_1^2 + V_1^2 + W_1^2$$
,  $C_2^2 = U_2^2 + V_2^2 + W_2^2$ .

The mean energy of the motion (U, V, W) "peculiar" to each molecule is clearly  $\frac{1}{2}m\overline{C}$  per molecule, and we write

$$m_1\overline{C_1}^2 = 3/2h_1 = 3RT_1, \qquad m_2\overline{C_2}^2 = 3/2h_2 = 3RT_2,$$

where R is the universal gas-constant. These equations define h and T;  $T_1$ ,  $T_2$ , will be termed the "temperatures" of the component gases, which are not necessarily exactly equal, though all the departures of the gas from the uniform state will be supposed small. The mean hydrostatic pressures of the component and composite gases, and also  $h_0$  and  $T_0$  (the "temperature" of the composite gas) are defined by

$$p_{1} = \frac{1}{3}\nu_{1}m_{1}\overline{C_{1}^{2}} = \nu_{1}/2h_{1} = R\nu_{1}T_{1}, \quad p_{2} = \frac{1}{3}\nu_{2}m_{2}\overline{C_{2}^{3}} = \nu_{2}/2h_{2} = R\nu_{2}T_{2},$$

$$p_{0} = p_{1} + p_{2} = \nu_{1}/2h_{1} + \nu_{2}/2h_{2} = \nu_{0}/2h_{0} = R\nu_{0}T_{0}.$$
Clearly
$$T_{0} = \lambda_{1}T_{1} + \lambda_{2}T_{2}, \qquad 1/h_{0} = \lambda_{1}/h_{1} + \lambda_{2}/h_{2}.$$

The six pressure components  $p_{xx}$ ,  $p_{yy}$ ,  $p_{zz}$ ,  $p_{xy}$ ,  $p_{yz}$ ,  $p_{xz}$ , for the component and composite gases are similarly defined, e.g.,

$$(p_{xx})_0 = (p_{xx})_1 + (p_{xx})_2 = \nu_1 m_1 \overline{U_1}^2 + \nu_2 m_2 \overline{U_2}^2,$$
  

$$(p_{xy})_0 = (p_{xy})_1 + (p_{xy})_2 = \nu_1 m_1 \overline{U_1} \overline{V_1} + \nu_2 m_2 \overline{U_2} \overline{V_2}.$$

We also define  $T_0'$ ,  $p_0'$ ,  $h_0'$ , by the equations

$$T_{\theta'} = \lambda_1 \lambda_2 (T_1 - T_2), \qquad 1/h_{\theta'} = \lambda_1 \lambda_2 (1/h_1 - 1/h_2)$$

$$p_{\theta'} = \nu_{\theta}/2h_{\theta'} = \lambda_1 \lambda_2 (p_1/\lambda_1 - p_2/\lambda_2) = R\nu_{\theta} T_{\theta'}.$$

Evidently 
$$T_1 = T_0 + T_0'/\lambda'$$
,  $T_2 = T_0 - T_0'/\lambda_2$ ,

and  $T_0'$  is a measure of the difference between the temperatures of the component gases.

When the gas is uniform, so that  $c_0$ ,  $\lambda$ ,  $h_0$  are constant, while  $c_0$ ,  $h_0$ , P, are zero, the function f(U, V, W) representing the distribution of the components of velocity (U, V, W) among the molecules  $m_1$  or  $m_2$  assumes Maxwell's well known form:

$$[f_1(\mathbf{U}_1, \mathbf{V}_1, \mathbf{W}_1)]_0 = (h_0 m_1 / \pi)^{3/2} e^{-h_0 m_1 \mathbf{O}_1^2},$$
  

$$[f_2(\mathbf{U}_2, \mathbf{V}_2, \mathbf{W}_2)]_0 = (h_0 m_2 / \pi)^{3/2} e^{-h_0 m_2 \mathbf{C}_2^2}.$$

These clearly satisfy the necessary conditions

$$\iiint f(\mathbf{U}, \mathbf{V}, \mathbf{W}) d\mathbf{U} d\mathbf{V} d\mathbf{W} = 1, \qquad \iiint f(\mathbf{U}, \mathbf{V}, \mathbf{W}) C^2 d\mathbf{U} d\mathbf{V} d\mathbf{W} = 3/2 hm.$$

For the velocity distribution function in the slightly disturbed state we shall write

$$f_1(U_1, V_1, W_1) = [f_1]_0 [1 - \phi_1(U_1, V_1, W_1)],$$

where  $\phi_1$  is a function, of the first order of smallness, which remains to be determined.

Let  $Q_1$  be any function of the velocity components  $(u)_1$ ,  $(v)_1$ ,  $(w)_1$ , of a molecule  $m_1$ ; then  $\nu_1\overline{Q_1}$  is the aggregate value of  $Q_1$  summed over all the molecules in unit volume. The equation expressing the analysis of the rate of change of  $\nu_1\overline{Q_1}$  is called the "equation of transfer" of  $Q_1$ . It may readily be shown to be\*

$$\frac{\partial}{\partial t}(\nu_1\overline{Q_1}) = \Delta Q_1 + \sum_{z,y,z} \left[ \frac{\partial}{\partial x}(\nu_1(\overline{u)_1}\overline{Q_1}) - \frac{\nu_1}{m_1} X_1 \overline{\left(\frac{\partial Q_1}{\partial (u)_1}\right)} \right].$$

The rate of change is here analysed into (a) the part  $\Delta Q_1$  due to the encounters between the molecules  $m_1$  among themselves or with the others  $m_2$ , (b) the part due to the passage of molecules into or out of the volume considered, and (3) that caused by the action of external forces.

By assigning to Q the values unity, (u), or  $(c)^2$ , we may obtain the equations of continuity, momentum, or energy, for the composite gas, since in these three cases, by virtue of the conservation of mass, momentum, and energy, we may eliminate  $\Delta Q$ .

Three special functions Q are important in the present theory. By means of the three equations just mentioned, and by the neglect of all second-order

<sup>\*</sup> Cf. Jeans' Dynamical Theory of Gases,' § 335 (2nd ed.).

quantities, the corresponding equations of transfer may be reduced to the following form:---

$$\begin{split} &\frac{3\left(2h_0m_1\right)^s}{1\cdot 3\dots (2s+3)}m_1\Delta U_1C_1^{2s} = \nu_0\xi_0' + Rs\nu_1\frac{\partial T_0}{\partial x},\\ &\frac{3\left(2h_0m_2\right)^s}{1\cdot 3\dots (2s+3)}m_2\Delta U_2C_2^{2s} = -\nu_0\xi_0' + Rs\nu_2\frac{\partial T_0}{\partial x},\\ &\frac{(2h_0m_1)^s}{1\cdot 3\dots (2s+1)}\Delta C_1^{2s} = \nu_0\frac{\partial \lambda_0'}{\partial t} = -\frac{(2h_0m_2)^s}{1\cdot 3\dots (2s+1)}\Delta C_2^{2s},\\ &\frac{3\left(2h_0m_1\right)^{s+1}}{1\cdot 3\dots (2s+3)}\Delta U_1^{2s}C_1^{2s} = \nu_0\frac{\partial \lambda_0'}{\partial t} + \frac{2}{15}\left(2s+5\right)\nu_1c_{xx},\\ &\frac{3\left(2h_0m_2\right)^{s+1}}{1\cdot 3\dots (2s+3)}\Delta U_2^{2c}C_2^{2s} = -\nu_0\frac{\partial \lambda_0'}{\partial t} + \frac{2}{15}\left(2s+5\right)\nu_2c_{xx},\\ &\frac{3\left(2h_0m_2\right)^{s+1}}{1\cdot 3\dots (2s+3)}\Delta U_2^{2c}C_2^{2s} = -\nu_0\frac{\partial \lambda_0'}{\partial t} + \frac{2}{15}\left(2s+5\right)\nu_2c_{xx},\\ &\frac{3\left(2h_0m_2\right)^{s+1}}{1\cdot 3\dots (2s+3)}\frac{1}{\nu_1}\Delta V_1W_1C_1^{2s} = \frac{2}{15}\left(2s+5\right)c_{yz} = \frac{3\left(2h_0m_2\right)^{s+1}}{1\cdot 3\dots (2s+3)}\frac{1}{\nu_2}\Delta V_2W_2C_2^{2s}. \end{split}$$

The following equations define  $\xi_0'$ ,  $c_{xx}$ ,  $c_{xy}$ , and there are, of course, similar quantities  $\eta_0'$ ,  $\xi_0'$ ,  $c_{yy}$ , and so on, which are defined in like manner:

$$\xi_{0}' = \frac{1}{2h_{0}} \frac{\partial \lambda_{0}'}{\partial x} - X_{0}' - \frac{m_{0}'}{\nu_{0}m_{0}} \frac{\partial p_{0}}{\partial x},$$

$$c_{xx} = 2\partial u_{0}/\partial x - \partial v_{0}/\partial y - \partial w_{0}/\partial z, \qquad c_{yx} = \frac{3}{2} (\partial v_{0}/\partial z + \partial w_{0}/\partial y).$$

In each of the above equations of transfer, as written, a multiple of  $\Delta Q$  is equated to certain "external" or mean data of the gas. The reduction to this form requires no knowledge of the small deviation from Maxwell's distribution law of molecular velocities, i.e., of the function  $\phi(U, V, W)$ , but such knowledge is necessary for the calculation of  $\Delta Q$ . Conversely, however, the above equations for  $\Delta Q$  throw light on the form of  $\phi(U, V, W)$ ; in fact, if we assume that  $\phi$  can be expressed as a power series in U, V, W, we may in this way\* infer that it will have the following form:—

$$\begin{aligned} \phi_{1}\left(\mathbf{U}_{1},\,\mathbf{V}_{1}\mathbf{W}_{1}\right) &= \frac{1}{3}\,2h_{0}m_{1}\mathbf{A}_{0}\left(\mathbf{U}_{1}\boldsymbol{\xi}_{0}'+\mathbf{V}_{1}\eta_{0}'+\mathbf{W}_{1}\boldsymbol{\xi}_{0}'\right)\,\mathbf{F}_{1}\left(\mathbf{C}_{1}^{2}\right) \\ &+ \frac{1}{3}\,2h_{0}m_{1}\mathbf{B}_{0}\left(\mathbf{U}_{1}\partial\mathbf{T}_{0}/\partial\boldsymbol{x}+\mathbf{V}_{1}\partial\mathbf{T}_{0}/\partial\boldsymbol{y}+\mathbf{W}_{1}\partial\mathbf{T}_{0}/\partial\boldsymbol{z}\right)\,\mathbf{G}_{1}\left(\mathbf{C}_{1}^{2}\right) \\ &+ \frac{2}{45}\,2h_{0}m_{1}\mathbf{C}_{0}\left(\boldsymbol{c}_{xx}\mathbf{U}_{1}^{2}+\ldots+2\boldsymbol{c}_{yx}\mathbf{V}_{1}\mathbf{W}_{1}+\ldots\right)\,\mathbf{H}_{1}\left(\mathbf{C}_{1}^{2}\right)+\mathbf{D}_{0}\,\partial\lambda_{0}'/\partial\boldsymbol{t}\,\,.\,\,\mathbf{J}_{1}\left(\mathbf{C}_{1}^{2}\right). \end{aligned}$$

The function  $\phi_2$  is obtainable by changing the suffix 1 into 2 throughout. We express the functions  $F(C^2)$ , etc., in power series which are conveniently written as follows:—

<sup>\*</sup> The details of the deduction will be found in the original papers, where it is shown how  $\Delta Q$  depends on  $\phi(U, V, W)$ .

$$\begin{split} \mathbf{F}_{1}\left(\mathbf{C}_{1}^{2}\right) &= \sum_{r=0}^{\infty} \alpha_{r} \frac{(2h_{0}m_{1})^{r}}{1 \cdot 3 \dots (2r+3)} \mathbf{C}_{1}^{2r}, \qquad \overset{\bullet}{\mathbf{G}}_{1}\left(\mathbf{C}_{1}^{2}\right) = \sum_{r=0}^{\infty'} \beta_{r} \frac{(2h_{0}m_{1})^{r}}{1 \cdot 3 \dots (2r+3) \cdot r} \mathbf{C}_{1}^{2r}, \\ \mathbf{H}_{1}\left(\mathbf{C}_{1}^{2}\right) &= \sum_{r=0}^{\infty} \gamma_{r} \frac{(2h_{0}m_{1})^{r}}{1 \cdot 3 \dots (2r+5)} \mathbf{C}_{1}^{2r}, \qquad \mathbf{J}_{1}\left(\mathbf{C}_{1}^{2}\right) = \sum_{r=0}^{\infty} \delta_{r} \frac{(2h_{0}m_{1})^{r}}{1 \cdot 3 \dots (2r+1)} \mathbf{C}_{1}^{2r}. \end{split}$$

The dash (') after the sign of summation in G (C<sup>9</sup>) is to indicate that r is to be omitted from the numerical factor of the first term (r = 0). These factors are arbitrary and not really necessary, since the coefficients  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  are unknown, but their insertion is analytically advantageous. Similarly it is convenient to denote the coefficients in  $F_2(C_2^2)$ , etc. (which expressions correspond to  $F_1(C_1^2)$ , etc., apart from the natural change of suffix) by  $\alpha_{-r}$ ,  $\beta_{-r}$ ,  $\gamma_{-r}$ ,  $\delta_{-r}$ ; it is then necessary to distinguish between  $\alpha_r$  and  $\alpha_{-r}$ , and so on, even when r = 0.

The factors  $A_0$ ,  $B_0$ ,  $C_0$ ,  $D_0$ , in  $\phi$  can be chosen at will, after which the coefficients  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ , become definite; these remain to be determined. Certain relations between them, however, hold good, in virtue of the conditions

$$\iiint f(\mathbf{U}, \mathbf{V}, \mathbf{W}) d\mathbf{U} d\mathbf{V} d\mathbf{W} = 1, \quad \iiint f(\mathbf{U}, \mathbf{V}, \mathbf{W}) C^2 d\mathbf{U} d\mathbf{V} d\mathbf{W} = 3/2\hbar m,$$
$$\iiint f(\mathbf{U}, \mathbf{V}, \mathbf{W}) \mathbf{U} d\mathbf{U} d\mathbf{V} d\mathbf{W} = u - u_n,$$

which (with the proper suffixes appended)  $f_1(U_1, V_1, W_1)$  and  $f_2(U_2, V_2, W_2)$  must clearly satisfy. These are readily seen to yield the equations:

$$\sum_{r=0}^{\infty} \delta_r = \sum_{r=0}^{\infty} \delta_{-r} = 0,$$

$$\lambda_1 \sum_{r=0}^{\infty} (2r+3) \delta_r = -\lambda_2 \sum_{r=0}^{\infty} (2r+3) \delta_{-r} = -3T_0'/D_0 (\partial \lambda_0'/\partial t),$$

$$\frac{1}{9} \lambda_1 \left\{ \Lambda_0 \xi_0' \sum_{0}^{\infty} \alpha_r + B_0 (\partial T_0/\partial v) \sum_{r=0}^{\infty'} r^{-1} \beta_r \right\}$$

$$= -\frac{1}{9} \lambda_2 \left\{ \Lambda_0 \xi_0' \sum_{r=0}^{\infty} \alpha_{-r} + B_0 (\partial T_0/\partial v) \sum_{r=0}^{\infty'} r^{-1} \beta_r \right\} = -u_0'.$$

In the last equation,  $\xi_0'$  and  $\partial \Gamma_0/\partial v$  are entirely independent quantities; hence, if we eliminate  $u_0'$ , we can separately equate their co-factors to zero, in the resulting equation. In this way the above equations may be re-written

$$\lambda_{1} \sum_{0}^{\infty} \alpha_{r} = -\lambda_{2} \sum_{0}^{\infty} \alpha_{-r} \equiv -\alpha_{0}',$$

$$\lambda_{1} \sum_{0}^{\infty} r^{-1} \beta_{r} = -\lambda_{2} \sum_{0}^{\infty} r^{-1} \beta_{-r} \equiv -\beta_{0}',$$

$$2\lambda_{1} \sum_{1}^{\infty} r \delta_{r} = -2\lambda_{2} \sum_{1}^{\infty} r \delta_{-r} \equiv -\delta_{0}',$$

which also define  $\alpha_0'$ ,  $\beta_0'$ , and  $\delta_0'$ ; consequently, also  $u_0' = \frac{1}{2} (\alpha_0' \mathbf{A}_0 \boldsymbol{\xi}_0' + \boldsymbol{\beta}_0' \mathbf{B}_0 \partial \mathbf{T}_0 / \partial r),$  $\mathbf{T}_0' = \frac{1}{2} \delta_0' \mathbf{D}_0 \mathbf{T}_0 \partial \lambda_0' / \partial t.$ 

#### (4) Determination of the Coefficients a, β, γ, ∂.

By means of the above expression for f(U, V, W) it is possible to calculate  $\Delta Q$ , the operation (a lengthy and elaborate one) consisting in the evaluation of an octuple integral involving the eight variables which are required to specify an encounter between two molecules. Small quantities of order higher than the first are neglected, and the resulting expression for  $\Delta Q$  always consists of a linear series of the coefficients  $\alpha_r$ ,  $\beta_r$ ,  $\gamma_r$ ,  $\delta_r$ , multiplied respectively into  $\xi_0'$ ,  $\partial T_0/\partial x$ ,  $e_{xx}$ ,  $\partial \lambda_0'/\partial t$ , etc.; the factor of each term in these linear series depends only on  $\nu$ ,  $h_0$ , and m, and involves the law of molecular interaction during encounter. It is found possible to obtain perfectly general expressions for these factors, i.e., no particular law of interaction has to be assumed.

On inserting the values of  $\Delta Q$ , so calculated, in the above equations of transfer, we may separately equate the parts on the two sides which contain  $\xi_0'$ ,  $\partial T_0/\partial x$ ,  $c_{xx}$ , or  $\partial \lambda_0'/\partial t$ . We thus obtain a number of equations, each of which is linear in one set only of the coefficients  $\alpha_r$ ,  $\beta_r$ ,  $\gamma_r$ , or  $\delta_r$ , the factors being as above stated, viz., definitely known functions of  $\nu$ ,  $h_0$ , and m. There is an infinite sequence of such equations for each set of coefficients, one equation corresponding to each value of s, which takes all integral values from 0 to  $\infty$ . If we solve them in the same way as for p linear equations in p unknowns, although p is here infinite, we arrive at solutions typified by the equation

$$\alpha_r = \frac{\nabla_r (a_{mn})}{\nabla (a_{mn})};$$

here  $a_{mn}$  denotes the coefficient of  $a_m$  in the *n*th equation of the sequence of equations for the a's (i.e., s=n), and  $\nabla(a_{mn})$  denotes the infinite determinant whose general element is  $a_{mn}$ , while  $\nabla_r(a_{mn})$  denotes the same determinant with the elements of column m=r all replaced by unity. These determinants are infinite in both directions, covering the whole plane; in each of the equations whence they are derived, m ranges from  $-\infty$  to  $+\infty$ , while the equations of transfer for  $\Delta Q_2$  provide a second infinite sequence of equations corresponding to the range of n from -0 to  $-\infty$ . If we are considering only a simple gas, so that  $\nu_2=0$ ,  $\phi_2$  and  $\Delta Q_2$  do not appear, and the determinants reduce to the more ordinary form, covering only a quadrant of the plane.

These general formulæ for the coefficients  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ , complete the determination of the velocity distribution function f(U, V, W). The mean value of any function of U, V, W, can hence be calculated in the form of a linear series of these coefficients. It remains only to add that any such linear series in the  $\alpha$ 's,  $\beta$ 's,  $\gamma$ 's, or  $\delta$ 's can readily be transformed into the quotient of an appropriate single determinant by  $\nabla$   $(a_{mn})$ ,  $\nabla$   $(b_{mn})$ ,  $\nabla$   $(c_{mn})$ , or  $\nabla$   $(a_{mn})$  respectively.

PART II.—APPLICATION TO THE THEORY OF THE MEAN-FREE-PATH PHENOMENA.

(1) Viscosity.

By I (1) and I (2), the total pressure components  $(p_{xx})_0$ ,  $(p_{xy})_0$ , are given by

$$(p_{xx})_0 = \nu_1 m_1 \overline{\mathbf{U}_1^2} + \nu_2 m_2 \overline{\mathbf{U}_2^2} = p_0 - \frac{4}{675} \frac{1}{2h_0} C_0 \left\{ \sum_{n=0}^{\infty} (\nu_1 \gamma_n + \nu_2 \gamma_{-n}) \right\} c_{xx},$$

$$(p_{xy})_0 = \nu_1 m_1 \overline{U_1 V_1} + \nu_2 m_2 \overline{U_2 V_2} = -\frac{4}{675} \frac{1}{2h_0} C_0 \{ \sum_{n=0}^{\infty} (\nu_1 \gamma_r + \nu_2 \gamma_{-r}) \} c_{xy}$$

Remembering the significance of  $c_{xx}$  and  $c_{xy}$ , and comparing these equations with the equations of pressure of a gas whose coefficient of viscosity is  $\kappa_{12}$ , viz., with

$$(p_{xx})_0 = p_0 - \frac{9}{3} \kappa_{12} c_{xx}, \qquad (p_{xy})_0 = -\frac{9}{3} \kappa_{12} c_{xy},$$

it is clear that the composite gas behaves like a viscous fluid, and that

$$\kappa_{12} = \frac{2}{225} \frac{C_0}{2h_0} \sum_{0}^{\infty} (\nu_1 \gamma_r + \nu_2 \gamma_{-r}).$$

(2) Diffusion.

From I (3), remembering the significance of  $\xi_0$ , it appears that

$$u_0' = \lambda_1 (u_1 - u_0) = -\lambda_2 (u_2 - u_0) = \lambda_1 \lambda_2 (u_1 - u_2)$$

$$= \frac{1}{9} A_0 \alpha_0' \left( \frac{1}{2h_0} \frac{\partial \lambda_0'}{\partial x} - X_0' - \frac{m_0'}{\nu_0 m_0} \frac{\partial p_0}{\partial x} \right) + \frac{1}{9} B_0 \beta_0' \frac{\partial T_0}{\partial x}.$$

Hence (taking the right-hand terms in order) diffusion is produced by (1) a concentration gradient, or variation in the relative proportions of the constituent gases; (2) by external forces acting unequally per unit mass on the two sets of molecules, and by variations in (3) the total pressure, or (4) temperature of the composite gas. If we write

 $D_{12} = -\frac{1}{9} A_0 R T_0 \alpha_0', \quad D_{12}' = D_{12}/p_0, \quad D_p = (m_0'/m_0) D_{12}, \quad D_T = -\frac{1}{9} B_0 \beta_0' T_0,$  then

$$u_0' = -\mathbf{D}_{12} \partial \lambda_0' / \partial x + \mathbf{D}_{12}' \nu_0 \mathbf{X}_0' + \mathbf{D}_p \cdot \partial p_0 / p_0 \partial x - \mathbf{D}_T \cdot \partial \mathbf{T}_0 / \mathbf{T}_0 \partial x,$$

and we may call  $D_{12}$ ,  $D_{12}$ ,  $D_{2}$ , and  $D_{T}$  respectively the coefficients of diffusion, forced diffusion, pressure diffusion, and thermal diffusion. The definition of  $D_{12}$  agrees with that usually given for the coefficient of diffusion. The other coefficients seem to be defined here for the first time.

If, as we have supposed, the molecules  $m_1$  are the heavier, the four coefficients of diffusion are positive. Hence, in the case of pressure diffusion, the heavier gas will tend towards the direction of increasing pressure; in the case of thermal diffusion, the heavier gas will tend towards the direction of decreasing temperature. Evidently both pressure and thermal diffusion will in general take place during the passage of sound through a composite gas such as air, the effects presumably being comparable with those of viscosity and conduction which have been investigated by Stokes, Kirchhoff, and Rayleigh.

#### (3) The Transfer of Energy by Conduction, Diffusion, Etc.

The equation of energy is the equation of transfer of  $\frac{1}{2}mC^2$ . On combining the separate equations for the two gas-components, the equation of energy for the whole gas, correct to the first order, is found to be

$$\begin{split} \rho_0 \mathbf{C}_v \frac{\mathbf{D} \mathbf{T}_0}{\mathbf{D} t} + \frac{2}{3} \rho_0 \mathbf{C}_v \mathbf{T}_0 \left( \frac{\partial u_0}{\partial v} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z} \right) \\ &= \frac{1}{J} \mathbf{\Sigma} v_0 u_0' \left\{ \left( \mathbf{X}_1 - m_1 \frac{\mathbf{D} u_0}{\mathbf{D} t} \right) - \left( \mathbf{X}_2 - m_2 \frac{\mathbf{D} u_0}{\mathbf{D} t} \right) \right\} \\ &+ \frac{1}{2} \frac{v_0}{J} (m_1 - m_2) c_0^2 \left( \frac{\partial u_0'}{\partial x} + \frac{\partial v_0'}{\partial y} + \frac{\partial w_0'}{\partial z} \right) \\ &+ \frac{\kappa_{12}}{J} \left\{ 2 \mathbf{\Sigma} \left( \frac{\partial u_0}{\partial x} \right)^2 + \mathbf{\Sigma} \left( \frac{\partial w_0}{\partial y} + \frac{\partial v_0}{\partial z} \right)^2 - \frac{2}{3} \left( \mathbf{\Sigma} \frac{\partial u_0}{\partial x} \right)^2 \right\} \\ &- \frac{1}{J} \mathbf{\Sigma} \frac{\partial}{\partial x} \left( \frac{1}{2} \rho_1 \overline{\mathbf{U}_1 \overline{\mathbf{C}_1}}^2 + \frac{1}{2} \rho_2 \overline{\mathbf{U}_2 \overline{\mathbf{C}_2}}^2 \right). \end{split}$$

Here  $C_v$  is the specific heat at constant volume, and J is Joule's mechanical equivalent of heat. The right-hand terms, it will appear, depend on viscosity, diffusion, and conduction. If we neglect these small effects, the equation may be written

$$\frac{1}{T_0}\frac{DT_0}{Dt} + \frac{3}{8}\left(\frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z}\right) = 0,$$

or, by the equation of continuity,

$$\frac{1}{T_0} \frac{DT_0}{Dt} - \frac{3}{3} \frac{1}{\nu_0} \frac{D\nu_0^2}{Dt} = 0, \quad \text{or} \quad \frac{D}{Dt} (T_0 \nu_0^{-\frac{3}{2}}) = 0, \quad \text{or} \quad \frac{D}{Dt} (p_0 \nu_0^{-\frac{3}{2}}) = 0.$$

This is the law of adiabatic expansion of a monatomic gas. The neglected

terms hence give the necessary corrections to this law, which are due to the causes indicated. The left-hand side represents the net rate of increase of energy of molecular agitation, being the increase corresponding to the rising temperature after allowing for the change due to adiabatic alteration of volume. This net rate is analysed as follows, taking the various terms in order:—

- (a) Work is done on the molecules by the external forces, in the motion of interdiffusion relative to the resultant stream velocity  $c_0$ .
- (b) The variation in the proportions of the molecules  $m_1$  and  $m_2$ , due to diffusion, produces a flow of energy of stream-motion  $c_0$ , since  $\frac{1}{2}m_1c_0^2$  exceeds  $\frac{1}{2}m_2c_0^2$ .
- (c) The viscous forces cause dissipation of energy, represented by the third term on the right-hand side.
- (d) The fourth term represents the effect of conduction, together with a hitherto unrecognised term due to diffusion. Supposing, for simplicity, that there is no mass motion, the equation of energy becomes

$$\begin{split} \rho_{\theta} C_{v} \frac{\partial T_{\theta}}{\partial t} &= \frac{1}{J} \sum \nu_{\theta} u_{\theta'} \left( X_{1} - X_{2} \right) + \frac{1}{\theta} \sum \frac{\partial}{\partial v} \frac{RT_{\theta}}{J} \left[ \frac{\sum_{i=1}^{\infty} r \left( \nu_{1} \alpha_{r} + \nu_{2} \alpha_{-r} \right)}{\alpha_{\theta'}} u_{\theta'} + \frac{1}{\theta} \frac{RT_{\theta}}{R} \left\{ \sum_{i=1}^{\infty} \left( \nu_{1} \beta_{r} + \nu_{2} \beta_{-r} \right) - \frac{1}{\theta} \frac{RT_{\theta}}{R} \sum_{i=1}^{\infty} r \left( \nu_{1} \alpha_{r} + \nu_{2} \alpha_{-r} \right) \right\} \right] \end{split}$$

on substituting the values of  $\overline{U_1C_1}^2$  and  $\overline{U_2C_2}^2$ , and substituting for  $\xi_0'$  in terms of  $u_0'$  and  $\partial T_0/\partial x$ . If, further, there is no diffusion, it reduces to the equation of conduction of heat with thermal conductivity 9, viz.,

$$\rho_0 C_v \frac{\partial T_0}{\partial t} = \Sigma \frac{\partial}{\partial x} \left( \Im \frac{\partial T_0}{\partial x} \right),$$

where

$$9 = \frac{1}{9} B_0 \frac{RT_0}{J} \left\{ \sum_{1}^{\infty} \left( \nu_1 \beta_r + \nu_2 \beta_{-r} \right) - \frac{\beta_0}{\alpha_0} \sum_{1}^{\infty} r \left( \nu_1 \alpha_r + \nu_2 \alpha_{-r} \right) \right\}.$$

It appears also that the motion of interdiffusion is accompanied by a flow of heat proportional to the velocity of diffusion, a process which we shall term the "thermal flux of diffusion." In the absence of conduction, external forces, and mass motion, the equation of energy is thus seen to be

$$\rho_0 C_r \frac{\partial \mathbf{T}_0}{\partial v} = \mathbf{\Sigma} \frac{\partial}{\partial v} (\mathbf{D} u_0'),$$

where **B** is defined by

$$\mathbf{m} = \frac{\mathbf{R}\mathbf{T}_0}{\mathbf{J}} \frac{1}{\alpha_0}, \mathbf{\Sigma}_1 r(\nu_1 \alpha_r + \nu_2 \alpha_{-r}),$$

and is called the "specific energy of diffusion."

(4) The Inequality of the Partial Temperatures.

In I (3) we found that

$$T_0' = \frac{1}{4} D_0 \delta_0' T_0 \partial \lambda_0' / \partial t$$

so that the temperatures of the component gases are unequal by an amount proportional to the rate of change of the ratio of their densities. We will write the equation in the form

$$T_{0}' = -I_{\lambda} \partial \lambda_{0}' / \partial t, \qquad I_{\lambda} \equiv -\frac{1}{3} D_{0} \delta_{0}' T_{0},$$

 $I_{\lambda}$  being termed the anisothermal constant of diffusion. Since  $I_{\lambda}$  is found to be positive, the gas of diminishing relative density is the hotter.

l'ART III.-DISCUSSION OF THE RESULTS IN VARIOUS SPECIAL CASES.

(1) Introductory Remarks and Notation.

The various results arrived at in Part II are complete and perfectly general. To be of service to natural philosophy, however, we must consider their values for selected particular molecular models, and in order to obtain numerical results we must be prepared to make successive approximations to the accurate formulæ. Our usual procedure in this Abstract will be to state the general form of the first approximation, and to determine the correction due to further approximations only for special types of molecule. The types which will be dealt with are (a) point centres of force varying inversely as the nth power of the mutual distance; (b) rigid elastic spheres; and (c) rigid elastic spheres surrounded by a field of attractive force.

The following notation must first be explained, in order that the formulæ of this section may be understood.

$$\mu_1 \equiv m_1/(m_1+m_2), \quad \mu_2 \equiv m_2/(m_1+m_2), \quad \mu_{12} \equiv m_1/m_2 = \mu_1/\mu_2 \equiv 1/\mu_{21},$$

$$\phi_{12}^k(y) \equiv (2k+1) \{\mu_1\mu_2h_0(m_1+m_2)\}^{-\frac{1}{2}} y \int_0^{\infty} \{1 - P_k(\cos\theta_{12})\} p \, dp.$$

Here  $\theta_{12}$  is the angle through which the relative velocity of two molecules,  $m_1$ ,  $m_2$ , is changed, during an encounter in which p is the distance between their initial or final lines of undisturbed rectilinear motion, and  $[(m_1+m_2)/h_0m_1m_2)]^{\frac{1}{2}}y$  is the magnitude of their initial or final relative velocity;  $P_k(\cos\theta_{12})$  is the Legendre function of  $\cos\theta_{12}$ , of degree k. If both molecules are of the same kind,  $m_1$  or  $m_2$ , the function corresponding to  $\phi_{12}^k(y)$  is written  $\phi_{11}^k(y)$  or  $\phi_{22}^k(y)$ . In the next equation,

$$\mathbf{K}^{k}(t) \equiv \frac{4\pi^{-\frac{1}{2}}}{(t+k+\frac{1}{2})_{t+k}} \int_{0}^{\infty} e^{-y^{2}} \phi^{k}(y) \, y^{2(t+k+1)} dy,$$

 $K^k(t)$  is affected by the same suffixes as the function  $\phi^k(y)$  under the

integral sign; K and  $\phi$  clearly depend upon the molecular model adopted, the various models differing in respect of the dependence of  $\theta_{12}$  on p and y. Again,

 $k_t \equiv K_{12}^{-1}(t)/K_{12}^{-1}(0), \qquad k^{(t)} \equiv K^2(t)/K_{12}^{-1}(0);$ 

in the latter the suffixes 11, 12, or 22, are to be added to correspond to the suffixes of  $K^2(t)$  on the left.

#### (2) Particular Molecular Models.

If the molecules are rigid elastic spheres of radii  $\sigma_1$ ,  $\sigma_2$ , it may readily be shown that

$$\mathbf{K}_{12}^{1}(0) = 4(\sigma_1 + \sigma_2)^2 \left(\frac{m_1 + m_2}{h_0 \pi m_1 m_2}\right)^{\frac{1}{6}},$$

$$k_t = (t+2)_t/(t+\frac{3}{2})_t, \quad k_{11}^{(t)} = \left[2\sigma_1/(\sigma_1+\sigma_2)\right]^2 k_{12}^t, \quad k_{22}^{(t)} = \left[2\sigma_2/(\sigma_1+\sigma_2)\right]^2 k_{12}^t, \\ k_{12}^{(t)} = \frac{5}{2}(t+3)_{t+1}/(t+\frac{5}{2})_{t+1}.$$

In these formulæ  $(t+2)_t$ , or, more generally,  $r_t$ , where t but not necessarily r is a positive integer, denotes r(r-1)...(r-t+1).

When the molecules are *n*th power centres of force, the force at unit distance being  $K_{12}m_1m_2$ , it may be shown that

$$\begin{split} \mathbf{K}_{12}^{1}(0) &= \frac{2}{\pi^{3/2}} \, \mathbf{I}_{1}(n) \left( \frac{h_{0} m_{1} m_{2}}{m_{1} + m_{2}} \right)^{2/(n-1) - \frac{1}{2}} [\mathbf{K}_{12}(m_{1} + m_{2})]^{2/(n-1)} \Gamma \left( 3 - \frac{2}{n-1} \right), \\ k_{t} &= \frac{\Gamma \left[ t + 3 - 2/(n-1) \right]}{(t + \frac{3}{2})_{t} \, \Gamma \left[ (3 - 2/(n-1)) \right]}, \\ k_{12}^{(t)} &= 5 \, \frac{\Gamma \left[ t + 4 - 2/(n+1) \right]}{(t + \frac{5}{2})_{t+1} \, \Gamma \left[ 3 - 2/(n-1) \right]} \frac{\mathbf{I}_{2}(n)}{\mathbf{I}_{1}(n)}, \\ k_{11}^{(t)} &= (\mathbf{K}_{11}/\mathbf{K}_{12})^{2/(n-1)} k_{12}^{t}, \qquad k_{22}^{(t)} &= (\mathbf{K}_{22}/\mathbf{K}_{12})^{2/(n-1)} k_{12}^{t}, \end{split}$$

where  $I_1(n)$ ,  $I_2(n)$ , are pure numbers, depending on n only.

When n = 5, so that the molecules are Maxwellian, we may note that  $k_t = 1$  for all values of t.

When the molecules are rigid elastic spheres surrounded by a field of attractive force, the latter may be allowed for very approximately by an additional factor  $(1+S_{12}/T)$  in  $K_{12}^{-1}(0)$ , a factor

$$\{1 + [2/(t+2)]S_{12}/T\}/(1 + S_{12}/T)$$

in  $k_t$ , and a factor  $\{1+[3/(t+3)]S/T\}/(1+S_{12}/T)$  in  $k^{(t)}$ . Here  $S_{12}$ , which is known as Sutherland's constant, t is given by

$$b_{19}^2 m_1 m_2 / 4 (m_1 + m_2) R$$
,

<sup>\*</sup> They are the same as the quantities thus denoted in Jeans' 'Dynamical Theory of Gases,' 2nd ed., §§305, st seq.

<sup>†</sup>  $S_{12}$  is Sutherland's diffusion constant; when the gas is simple,  $S_{12}$  becomes  $S_{11}$ , but Sutherland's constant of viscosity (generally written C) is  $\frac{2}{3}S_{11}$ , or  $b_{11}^{2}n_{1}/12R$ .

where  $\frac{1}{2}b_{13}^2$  is the potential of the force between two molecules  $m_1$ ,  $m_2$ , when in contact;  $S_{11}$  and  $S_{22}$  are similarly defined, and appear in the numerators of the additional factors in  $k_{11}^{(\ell)}$  and  $k_{22}^{(\ell)}$ .

By putting  $m_1 = m_2$ ,  $\nu_2 = 0$ , and changing the suffix 2 into 1 throughout, our formulæ for a composite gas reduce to those appropriate to a simple gas. We shall first deal with the latter.

#### (3) The Viscosity of a Simple Gas.

The general first approximation to the coefficient of viscosity  $\kappa_{11}$  of a simple gas is

 $5 \,\mathrm{RT}/\pi \,\kappa_{11}^2 (0)$ .

This result was given and discussed in an earlier memoir,\* so that only the correction introduced by further approximations need be considered here.

In the case of rigid elastic spherical molecules, the correction factor is purely numerical, as also in the case of nth power centres of force. Successive approximations to the factor in the former instance are found to be 101485, 101588, 101607, so that 1016 times the above result may be taken as exact to well within  $\frac{1}{2}$  per cent. For nth power centres of force, similarly, the correction factor is found to have the values 1000, 1004, 1007, 1011, 1016, corresponding to the typical values 5, 9, 15, 25 and infinity for n.

In the case of rigid elastic attracting molecules, the correction factor varies very slightly with temperature. Typical values, corresponding to the values  $\infty$ , 5, 3, 1, 0.4, 0.2, 0.1, 0 for S/T, are respectively 1.016, 1.010, 1.006, 1.000, 1.004, 1.014, and 1.015. Thus, in all cases, the first approximation is exceedingly close to the exact value.

#### (4) The Thermal Conductivity 911 of a Simple Gas.

A first approximation leads to the result

as given in the earlier memoir just cited. As in the case of viscosity, the correction consists of a numerical factor to be applied to the above result; this factor is very nearly unity, being 1.010 for rigid elastic spheres, and for nth power centres of force varying from 1.000 for n = 5, through the values 1.003, 1.006, 1.007 for n = 9, 15, and 25, to 1.010 for  $n = \infty$ . Similarly for attracting spheres, as S/T takes the values  $\infty$ , 5, 3, 1, 0.4, 0.2, 0.1, 0, the factor is found to equal 1.022, 1.007, 1.003, 1.000, 1.002, 1.003, 1.004, and 1.010 respectively. The corrections to the first approximation are

\* 'Phil. Trans.,' A, vol. 211, pp. 433-483, §§17, 20 (1911).

hardly within the present experimental powers of measurement, and the simple formula  $\frac{5}{2}\kappa_{11}C_v$  agrees well with the observed values for argon, helium, and neon.

The general first approximation to  $D_{19}$  is

$$3(m_1+m_2) RT/2\pi\nu_0 m_1 m_2 K_{12}^{-1}(0)$$
.

This result was first obtained by Langevin, and subsequently, independently, in the earlier memoir by the present author, already cited. Like the first approximations also to  $\kappa_{11}$ ,  $\theta_{11}$ , and  $\theta_{12}$ , it is an exact formula in the case of Maxwellian molecules, and in no other. Maxwell obtained this expression for  $\theta_{12}$  in his own special case, though without a rigorous proof; his method when applied to other cases (as by the authors named) leads only to the above first approximation, the error of which is in some cases considerable. We shall write the correction factor introduced on a second approximation in the form  $1/(1-\epsilon_0)$ . Before considering the value of  $\epsilon_0$  we shall examine some particular cases of our formulæ which throw light on the accuracy of a second approximation in general.

When the mass and size of the molecules  $m_2$  are negligible compared with those of  $m_1$ , an exact solution for  $D_{12}$  is obtainable, as Lorentz first showed. The first few approximations to the correction factor in this case, when the molecules are rigid elastic spheres, are found to be 1.083, 1.107, 1.117, converging to the value  $32/9\pi$  or 1.132. If the molecules are nth power centres of force, the correction factor is equal to

$$\frac{16}{9} \left(1 + \frac{2}{n-1}\right) \frac{2}{n-1} \left(1 - \frac{2}{n-1}\right) \left(2 - \frac{2}{n-1}\right) \frac{1}{\sin\left[2\pi/(n-1)\right]},$$

which, when n is 5, 9, 13, 17,  $\infty$ , has the respective values 1.000, 1.031, 1.056, 1.072, 1.132. These results agree with Lorentz's theory, and show that in this case, at any rate, the first approximation to  $D_{12}$  is seriously in error.

The next simplest case of a general character with which we can deal is that in which the molecules  $m_1$ ,  $m_2$  are identical in dynamical properties (e.g., mass, size, force), as, for instance, in the diffusion of a gas into itself. Hence we shall in this case write  $D_{11}$  for  $D_{12}$ . The correction factor is found to depend only on the nature of the molecule; its values for nth power centres of force, when n equals 5, 9, 17, or  $\infty$ , are respectively 1.000, 1.004, 1.008, or 1.015, and the last value also corresponds to rigid spherical molecules. These are only first approximations, but would not be altered by further approximations by more than 0.001 or 0.002. The complete formula for rigid spherical molecules is

$$0.1520/\nu_1 (2\sigma_1)^2 (h_1m_1)^{1/2}$$
.

The correction factor in this case had been previously calculated approximately by Pidduck, who obtained 0.151 (given thus to three decimal places only) in place of 0.1520 as above.

For the same type of molecule, we also have  $D_{11} = 1.200 \kappa_{11}/\rho_1$ , which may be compared with an approximate result obtained by Jeans, using the "mean-free-path" method, viz.,  $D_{11} = 1.34 \kappa_{11}/\rho_1$ . For other types of molecule,  $D_{11}$  is a different multiple of  $\kappa_{11}/\rho_1$ .

#### (6) Variation of D<sub>12</sub> with the Ratio of Mixture ν<sub>1</sub>/ν<sub>2</sub>.

The above first approximation to  $D_{12}$ , it may be noticed, depends only on  $\nu_1 + \nu_2$ , and not at all on the ratio  $\nu_1 : \nu_2$ . Meyer disputed the independence of  $D_{12}$  on the ratio of mixture, and developed a theory predicting considerable changes of  $D_{12}$  as  $\nu_1/\nu_2$  was varied. Experimental results showed a small variation of  $D_{12}$ , but much less than Meyer's formula alleged. This cast suspicion on both Maxwell's and Meyer's theories; it now appears that the former was correct, but failed to represent the facts because of the unsuitability of the molecular model. A Maxwellian gas is the only one for which  $D_{12}$  is independent of  $\nu_1/\nu_2$ . The correction factor to the above approximate formula is in every other case a function of  $\nu_1/\nu_2$ .

We shall consider only the approximation  $1/(1-\epsilon_0)$  to the correction factor; this is very nearly exact. We find that

$$\epsilon_0 = (k_1 - 1)^2 \frac{b_1 v_1^2 + 2 b_1 v_1 v_2 + b_2 v_2^2}{d_1 v_1^2 + 2 d_1 v_1 v_2 + d_2 v_2^2}$$

where

$$b_1 = 2 \mu_1 \mu_{12} k_{11}^0$$
,  $b_2 = 2 \mu_2 \mu_{12} k_{22}^0$ ,  $2b_{12} = 30 (1 - 4 \mu_1 \mu_2) + 8 \mu_1 \mu_2 k_{12}^0$ ,

$$d_1 = \frac{1}{\mu_2} k_{11}^0 \left\{ \frac{1}{5} \left( 1 - 2\mu_1 \mu_2 \right) + \frac{1}{2} \frac{6}{5} \mu_1 \mu_2 k_{12}^0 - 2 \left( \frac{1}{5} + 2k_1 - \frac{7}{5} k_2 \right) \mu_1^2 \right\},$$

$$2d_{12} = \frac{4}{25} \frac{1}{\mu_1 \mu_2} k_{11}^0 k_{22}^0 + \frac{a}{5} (1 - 4\mu_1 \mu_2) (1 - 2k_1 + \frac{7}{5}k_2) + 8\mu_1 \mu_2 k_{12}^0 (\frac{1}{5} - 2k_1 + \frac{7}{5}k_2),$$

and  $d_2$  is obtainable from  $d_1$  by interchanging the suffixes 1 and 2.

The behaviour of  $\epsilon_0$  with change of  $\nu_1/\nu_2$  is easily studied when the molecules are rigid elastic spheres. In this case (remembering the convention  $m_1 \gg m_2$ ) it appears that  $b_1/d_1$  exceeds  $b_2/d_2$ , and that  $b_{12}/d_{12}$  exceeds  $b_2/d_2$ . Further, if

$$\left\{\frac{4\sigma_1\sigma_3}{(\sigma_1+\sigma_2)^2}\right\}^2 > \frac{1}{4}\frac{\mu_2^3}{\mu_1}(1+80\,\mu_2-100\,\mu_1\mu_2),$$

we have  $b_1/d_1 > b_{12}/d_{12} > b_2/d_2$ ; the signs of equality correspond to the case  $m_1 = m_2$ ,  $\sigma_1 = \sigma_2$ , as in self diffusion. This indicates why  $D_{11}$  does not depend on  $\nu_1/\nu_2$ . In the general case, if the above condition is fulfilled,

 $\epsilon_0$  and  $1/(1-\epsilon_0)$  steadily decrease, as the proportion of molecules  $m_2$  is increased, while, if it is not fulfilled,  $\epsilon_0$  and  $1/(1-\epsilon_0)$  (and consequently also D<sub>12</sub>) first increases and then decreases, as  $\lambda_2$  increases from 0 to 1. Clearly, the more equal the molecular masses, the more equal also must be the molecular radii, in order that the above condition may be fulfilled.

As regards the magnitude of the correction factor, it is greater the more unequal the diameters and masses of the molecules, reaching a maximum of  $32/9\pi$ , or 1·132, when  $m_1/m_2$  and  $\sigma_1/\sigma_2$  are infinite. This is for rigid spherical molecules: for other types the range is less, shrinking to zero in the case of Maxwellian molecules. In other cases the factor appears always to exceed unity.

The magnitude of the variation in ordinary cases, and the comparison of experiment with theory, may be gauged from the following Table\*; the theoretical values of  $D_{12}$  are so calculated as to make their mean agree with the mean of the experimental values, so that the theory is concerned only with the variations from the mean. The molecules are assumed to be rigid spheres, though a less simple model might prove still better.

	ν,	Correction	D <sub>19</sub> .		
Gasen.	$\lambda_1 = \frac{\nu_1}{\nu_1 + \nu_2}$	factor,	Observed.	Calculated	
Argon and helium	0 .273	1 .050	0 244	0.248	
	0.815	1.056	0 .250	0 .250	
	0.377	1 .068	0 .250	0 .251	
	0.500	1 '073	0 .254	0 .254	
	0 .677	1.087	0 256	0 .257	
	0.768	1 '094	o <b>·2</b> 63	0 259	
Oxygen and hydrogen	0 .25	1 .050	0 .276	0 .276	
-,-	0.5	1 .078	0 :280	0 282	
	0.75	1 .097	0.289	0.289	

It may be added that Kuenen<sup>†</sup> has improved Meyer's theory of  $D_{12}$  by taking persistence of velocities into account, and has thus much reduced Meyer's predicted variations with  $\nu_1/\nu_2$ , though they still remain twice or thrice as great as the observed changes.

<sup>\*</sup> The observed data were obtained in the Halle Laboratory, under Prof. Dorn, by Schmidt, Deutsch, Jackmann, and Lonius ('Ann. d. Phys.,' vol. 29, p. 664, 1909).

<sup>†</sup> Kuenen, Supp. 8 to 'Leiden Phys. Comm.,' January, 1913.

(7) Thermal and Pressure Diffusion.

The first approximation to the coefficient of thermal diffusion D<sub>T</sub> is

$$\frac{3(m_1+m_2)\,\mathrm{RT}}{2\,\pi\nu_0m_1m_2\mathrm{K}_{12}{}^1(0)}\frac{(k_1-1)\,\epsilon_1}{\nu_0\,\Delta_1},$$

where

 $\epsilon_1 = 30 \left(\nu_1 \mu_2 + \nu_2 \mu_1\right) \left(\mu_1 - \mu_3\right) - 8\mu_1 \mu_2 k_{12}^0 \left(\nu_1 - \nu_2\right) + 2 \left(\nu_1 \mu_{12} k_{11}^0 - \nu_2 \mu_{21} k_{22}^0\right),$  and

$$\Delta_1 = (1/\nu_1\nu_2) \{ (d_1\nu_1^2 + 2d_{12}\nu_1\nu_2 + d_2\nu_2^2) - (k_1 - 1)^2 (b_1\nu_1^2 + 2b_{12}\nu_1\nu_2 + b_2\nu_2^2) \}.$$

In the case of Maxwellian molecules  $D_T$  vanishes (as also every approximation to it, as here, since  $k_1 = 1$  for such a gas); like the variation of  $D_{12}$  with  $\nu_1/\nu_2$ , thermal diffusion is a phenomenon which wholly disappears in this alone out of all typical gases, so that the model is far from suitable physically, whatever its mathematical advantages.

Thermal diffusion depends essentially on a difference of mass and structure between the molecules  $m_1$ ,  $m_2$ ; if  $m_1 = m_2$  and  $k_{11}{}^0 = k_{22}{}^0$ , etc.,  $D_T$  vanishes, as the above first approximation also suggests. The more unequal the molecules, the greater is  $D_T$ . Considering elastic spherical molecules, if  $\sigma_1 = \sigma_2$  but  $m_1/m_2$  is very large,  $D_T$  reduces approximately to

$$D_{12} \cdot 15\lambda_1\lambda_2/(39 + \lambda_2)$$

(thus if  $\lambda_1 = \lambda_2 = \frac{1}{2}$ ,  $D_T = 0.095 D_{12}$  nearly). When both  $m_1/m_2$  and  $\sigma_1/\sigma_2$  are very large (Lorentz's case)

$$D_{\rm T} = \frac{3\lambda_2}{16\nu_0(\sigma_1 + \sigma_2)^3 (\hbar\pi m_2)^{1/2}} \frac{{\rm D_1}'}{{\rm D}'},$$

where first, second, and third approximations to the numerical factor  $D_1'/D'$  give 0.417, 0.494, 0.524, converging to 0.58 nearly—this also illustrates the degree of correction introduced on further approximations after the first, although the error of the latter is at its maximum for this specially unequal molecular pair; the above formula is, moreover, true only so long as  $\lambda_2$  is not too nearly equal to 1, since  $D_T$  vanishes with  $\lambda_1\lambda_2$  always. If  $\lambda_1 = \lambda_2 = \frac{1}{2}$ , we get  $D_T = 0.26 D_{12}$  nearly, which may be compared with the former case when  $\sigma_1 = \sigma_2$ , as illustrating the effect of the inequality between the molecular diameters when  $m_1/m_2$  is very large.

Pressure diffusion likewise depends on the inequality of the molecules (of their masses only, however). Thus

$$\mathbf{D}_p = \mathbf{D}_{12} \cdot \lambda_1 \lambda_2 \left( m_1 - m_2 \right) / (\lambda_1 m_1 + \lambda_2 m_2).$$

The following Table illustrates the relative magnitudes of  $D_{12}$ ,  $D_{T}$  and  $D_{\rho}$  for a few typical gas-pairs (rigid elastic spherical molecules being assumed):—

Ratio of	$m_1/m_2 = 0.8  \sigma_1/\sigma_2 = 1.7.$			$m_1/m_2 = 16$ $\sigma_1/\sigma_2 = 1.3$ .			$m_1/m_2 = 1.1$ $\sigma_1/\sigma_2 = 1.0$ .		
ν1 : ν2.	Dr / D12.	D <sub>p</sub> / D <sub>12</sub> .	$\mathbf{D}_{\!p}/\mathbf{D}_{\!\mathbf{T}}$ .	D <sub>T</sub> / D <sub>12</sub> .	D <sub>p</sub> / D <sub>19</sub> .	$\mathrm{D}_{\!p}/\mathrm{D}_{\mathrm{T}}$ .	Dr / D12.	D <sub>p</sub> / D <sub>12</sub> .	$\mathbf{D}_{\!p}/\mathbf{D}_{\mathbf{T}}$ .
1:8 1:1 3:1	0 ·188 0 ·182 0 ·079	0 513 0 408 0 166	3 ·9 <b>3</b> ·1 <b>2</b> ·1	0 ·122 0 ·128 0 ·079	0 ·592 0 ·441 0 ·230	4.8 8.4 2.9	0 ·008 0 ·010 0 ·007	0 ·026 0 ·088 0 ·024	3 ·2 3 ·8 3 ·4

In this connection we may also remark on the steady state of a gas without diffusion, under the influence of (a) external forces or (b) of a permanently maintained non-uniform temperature distribution. former case the pressure will, of course, be non-uniform. The equations of diffusion show that a permanently non-uniform composition will thus be set up, depending in case (a) on the ratio  $D_{12}/D_{12}$  or  $D_p/D_{12}$ , and in (b) on D<sub>T</sub>/D<sub>12</sub>. Both cases are exemplified in the upper strata of the atmosphere, above the region of convection, and in a future note the effect of temperature gradient on atmospheric constitution will be indicated in detail; it is less, however, than the effect of the diminishing pressure. The influence of nonuniform temperature on composition has been verified experimentally, the proportions of two gases being found to differ in two bulbs kept at different temperatures and with an open connection between them; a preliminary account of these experiments will appear shortly. The magnitude of the effect is easily indicated by an example; if argon and helium, or oxygen and hydrogen, are the gases, mixed in originally equal proportions, and the hot bulb is kept at 100° C. and the cold at 0° C., the heavier gas will concentrate slightly in the cold bulb, 52 per cent. of it to 48 per cent. of the lighter gas, instead of the original 50 per cent. to 50 per cent., and vice versa at the hot bulb.

#### (8) Viscosity and Conduction in Mixed Gases.

The formulæ for  $\kappa_{12}$  and  $9_{12}$  in mixed gases are very complicated. A first approximation to  $\kappa_{12}$  agrees with that given in my first memoir, but the first approximation to  $9_{12}$  was there given wrongly, since, in deriving it, it was assumed that conduction could take place in a uniform gas without diffusion, which we have just seen to be impossible. The correct formula is given in the second memoir here abstracted, but will not be reproduced in this place.

#### (9) Inequality of the Temperatures of the Component Gases.

This phenomenon has been shown to depend on  $\partial \lambda_0'/\partial t$ , or the time rate of variation of the relative proportions of the component gases. The following

example will illustrate its order of magnitude. Consider a gas composed initially of equal numbers of molecules which are similar to one another in mass and other dynamical properties (since the phenomenon does not, like thermal diffusion, depend on molecular differences, this assumption may legitimately be made, in order to obtain a simple numerical illustration). We will suppose that the gas is at normal temperature and pressure, and that the molecules are similar in mass and size to oxygen molecules, though differing from one another in some other respects. Then if the proportions are changing at such a rate that at the end of one second there will be 51 per cent. of one component to 49 per cent. of the other, a temperature difference of about one thousand-millionth of a degree Centigrade will be set up, the hotter gas being that which is in diminishing ratio. Thus equipartition of energy is disturbed only by a negligible amount even in this rather extreme case.

On the Mechanical Relations of the Energy of Magnetisation.

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1. There still appears to be some uncertainty in the expression for the total energy of a magnetic field, and the mode of its separation into its fundamental constituents, as belonging to the æther and the matter. This is chiefly due to certain discrepancies of sign which exist in the results of the theory in its statical and dynamical aspects. In the statical theory the energy is usually made to appear as though distributed over the field with the density  $\mu H^2/8\pi$ , which corresponds to an æthereal density of amount  $H^2/8\pi$ , but in the dynamical theory the same expressions are obtained with opposite signs. In some quarters it is considered that there are difficulties of a fundamental nature involved in any attempt to remove this discrepancy, and several authors\* have tried to construct a more consistent theory on a new basis.

The object of the present note is mainly to prove that it is possible to interpret the older and more usual form of the theory in a perfectly logical and consistent manner, so that the aforementioned discrepancy does not

<sup>\*</sup> Cf. 'Encyclopädie der mathematischen Wissenschaften,' vol. 5, Art. 15, "Electrostatik u. Magnetostatik" (R. Gans), p. 338, where full references are given.

even present itself. It is shown that the whole difficulty arises partly from an unfortunate choice of ethereal vector, and partly also in the fact that the usual expression for the energy density in the statical case, although in complete agreement with the proper total, is not the proper expression to use in a consistent theory.

It has already been emphasised by Larmor\* that the magnetic induction vector is by far the more suitable vector to use in defining conditions in the magnetic field of the æther. In fact, in a strict theory, the magnetic induction is the fundamental vector, and the magnetic force is an auxiliary vector derived in the process of averaging the small molecular current whirls into their effective representation as a distribution of magnetic polarity. We therefore interpret all our results in terms of the magnetic induction, instead of the more usual magnetic force.

2. In the statical theory of magnetism, the energy involved in the magnetic polarisation in any stationary field is to be considered as the potential energy of the separate poles of the elementary magnets of which it is composed. This is easily seen to be equivalent to a distribution of amount per unit volume at any place equal to —(IH), wherein I is the averaged intensity of the polarisation produced at the place, and H is the intensity of force in the polarising field, which in the present instance may be regarded as derived from an acyclic potential.

Of this energy the part

$$-\int_0^{\mathbf{H}} (\mathbf{I}d\mathbf{H}),$$

is alone concerned with the mechanical bodily forces on the magnetic media, of which it may be regarded as the potential function. This follows in the usual manner from the principle of virtual work, which implies that the work done by such mechanical forces per unit volume in any small displacement of the body is  $-\delta$  (IH), wherein, however, the internal constitution of the medium, as specified in its polarisation, is to remain unaltered during the displacement, so that all the mechanical work is properly converted, and none of it runs off as energy of intrinsic deformation and consequently of effectively non-available character in the medium; or it may be deduced from the fact that the linear forcive per unit volume on the medium, calculated from first principles, is equal to  $-(I\nabla)H$ , wherein  $\nabla$  is the usual Hamiltonian vector operator.

\* Cf. his book 'Æther and Matter,' and also the paper "On the Electrodynamic and Thermal Relations of the Energy of Magnetisation," 'Roy. Soc. Proc.,' vol. 71, p. 229 (1904). The contents of this latter paper suggested the developments aketched in the present note.

The remaining part of the total energy, or

$$-\int_0^1 (HdI),$$

represents work done by the internal elastic or motional forces resisting the setting up of the polarisations. With sign changed it may be regarded as energy of effectively non-magnetic nature stored up in the medium on account of the polarisation induced in it.

3. Let us now examine the distribution of the total magnetic energy in the field on the supposition that it arises from a distribution of rigid magnetic polarity of density  $I_0$  at any point. The total energy may be calculated as the mechanical work done in building up the rigid magnetism gradually in the presence of the magnetisable substances, the induced magnetism simultaneously taking its appropriate value at any stage of the process. Suppose that at any instant the intensity of force at the typical field point is H, then the work supplied by external systems in bringing up an additional small increment of polarity  $\delta I_0$  to each place in the field is clearly equal to

$$-\int dv \, (H\delta I_0),$$

the integral being taken throughout the field.

Now by definition of H,

$$B = H + 4\pi (I + I_0),$$

where I is now reserved for the intensity of the induced polarity, so that

$$-(H\delta I_0) = (H\delta I) + (B\delta H)/4\pi - \delta \{B^2 - 16\pi^2(I + I_0)^2\}/8\pi.$$

Thus the total work done in establishing the field may be written in the form

$$\int \! dv \left[ -\frac{1}{8\pi} \left\{ \mathbf{B}^2 - 16\pi^2 (\mathbf{I} + \mathbf{I}_0)^2 \right\} + \int_0^1 \! (\mathbf{H}d\mathbf{I}) + \frac{1}{4\pi} \int_0^1 \! (\mathbf{B}d\mathbf{H}) \right].$$

But if there are no sudden discontinuities in the field, and any such might be treated as continuous rapid transitions, it is easy to prove\* that

$$\int (HB)dv = \int (H\delta B)dv = \int (B\delta H)dv = 0.$$

These follow in the usual way because the induction vector is always circuital, and the force vector in the present case is derived from an acyclic potential.

Thus the expression for the total energy in the field reduces to

$$-\frac{1}{8\pi}\int [B^2-16\pi^2(I+I_0)^2]dv + \int dv \int_0^1 (HdI).$$

\* Cf. Jeans, 'Electricity and Magnetism' (1st Ed.), p. 387.

The second integral in this last expression represents the internal elastic or motional energy stored up in the magnetic media on account of the polarity induced in them. The first integral therefore represents the true magnetic potential energy of the system, and on a tentative theory could now be regarded as distributed throughout the field with a density

$$-[B^2-16\pi^2(I+I_0)^2]/8\pi$$

at any place. Of this latter part of the energy the term in the polarisation represents energy of a purely local or intrinsic nature in the magnetic media, whilst the other term represents the part of the energy that must be associated with the field in the æther.

4. Of the true magnetic potential energy in the field, viz.,

$$-\frac{1}{8\pi}\int [B^2-16\pi^2(I+I_0)^2]\,dv,$$

the part

$$-\int dv \int_0^{\rm H} ({\rm I}d{\rm H})$$

corresponds to the polarisations induced in the magnetic media. It is concerned mainly with the magnetic attractions, or their equivalent mechanical forces, exerted by the field on the polarised media as a whole, of which it may be regarded as the potential function.

The remainder, or

$$-\frac{1}{8\pi}\int \left[B^2-16\pi^2(I+I_0)^2\right]dv+\int dv\int_0^H (IdH),$$

corresponds to the rigid polarisation and is, in fact, the potential function of the mechanical reactions on the permanent magnets giving rise to the field. Since

$$B = H + 4\pi (I + I_0),$$

this part may be written in the form

$$-\frac{1}{4\pi}\int dv \int_{0}^{\mathbf{B}} (\mathbf{H}d\mathbf{B}) - \int dv \int_{0}^{\mathbf{H}} (\mathbf{I}_{0}d\mathbf{H}),$$

which, since in every stage of the process

$$\int (\mathbf{H}d\mathbf{B})\,dv = 0,$$

reduces to

$$-\int dv \int_0^{\mathbf{H}} (\mathbf{I_0} d\mathbf{H})$$

in agreement with the result of §2.

5. When the induction follows a linear isotropic law, so that

$$B = \mu H + 4\pi I_0$$

we have

$$\mathbf{H} = (\mathbf{B} - 4\pi \mathbf{I}_0)/\mu,$$

and therefore

$$I = (\mu - 1) (B - 4\pi I_0)/4\pi\mu$$

and

$$I + I_0 = \{(\mu - 1) B + 4\pi I_0\}/4\pi\mu$$

In this case the energy stored in the magnetic media on account of the induced polarisation is

$$\int \frac{\mu - 1}{8\pi\mu^2} (B - 4\pi I_0)^2 dv,$$

whilst the energy of truly magnetic nature in the field is equal to the integral of

$$\begin{split} &-\mathrm{B}^2/8\pi + \{(\mu-1)\;\mathrm{B} + 4\pi\mathrm{I}_0\}^2/8\pi\mu^2 \\ &= -\left(\mathrm{B}^2 - 16\pi^2\mathrm{I}_0^2\right)/8\pi\mu - (\mu-1)\left(\mathrm{B} - 4\pi\mathrm{I}_0\right)^2/8\pi\mu^2. \end{split}$$

The total energy associated with the magnetic system is therefore simply equal to

$$-\frac{1}{8\pi}\int \frac{B^2-16\pi^2I_0^2}{\mu}dv,$$

and it may be regarded as distributed throughout the field with the density  $-B^2/8\pi\mu$  if the constant local part in  $I_0$  is omitted, as it would be in any mechanical theory. At points of the field where there is no rigid magnetism this density is the same as  $-\mu H^2/8\pi$ , which is the expression usually derived, but with the opposite sign. The difference of sign arises from the fact that in the usual interpretation of these relations an expression is adopted for the energy density which differs from that just deduced by  $(BH)/4\pi$ , giving a zero total on the whole.

6. We next turn to the consideration of the circumstances in the more general type of magnetic field when there are linear conduction currents as well as permanent magnets and magnetisable media. The work required in order to increase the typical current J in one of these conductors by the infinitesimal amount  $\delta J$  is

$$-\frac{1}{c}N\delta J$$

in electromagnetic units; N denotes the number of unit tubes of induction which thread the circuit of J. Thus the total energy supplied by the batteries in starting the currents is

$$-\sum_{c}^{1}\int_{0}^{J}NdJ = -\frac{1}{c}\sum_{c}\int_{0}^{J}dJ\int_{f}B_{n}df,$$

where  $\Sigma$  denotes a sum relative to the various linear currents and in the last expression the surface integral for each circuit is taken over a barrier surface

closing that circuit. In the usual case when the magnetic force is derivable from a potential cyclic with respect to the finite currents this expression is proved by the usual argument to be equivalent to the volume integral

$$-\frac{1}{4\pi}\int dv \int_0^{\rm H} ({\rm B}d{\rm H})$$

taken throughout the field.

If we include for generality a distribution of rigid magnetism throughout the field of intensity  $I_0$  at any point, and if we imagine this to be built up with the current system, an additional amount of work is done by the internal forces of the system equal to

$$= \int dv \int_0^{\mathbf{I_0}} (\mathbf{H} d\mathbf{I_0}).$$

Thus the total amount of energy stored up in the system is

$$= \frac{1}{4\pi} \int dr \bigg[ \int_0^{\mathbf{H}} (\mathbf{B}d\mathbf{H}) + 4\pi \int_0^{\mathbf{I}_0} (\mathbf{H}d\mathbf{I}_0) \bigg].$$

But if there are magnetisable substances about in the field, and if at any stage of the process of building up the system the intensity of the induced polarity is I, then

$$B = H + 4\pi (I + I_0)$$

It is then easy to prove that the total energy of the system can be expressed in the form

$$-\frac{1}{8\pi} \int \{B^2 - 16\pi^2 (I + I_0)^2\} dr + \int dr \int_0^1 (H dI).$$

The last term represents the increase in the intrinsic energy of the induced polarisations in the field and the first the increase of the purely magnetic energy. This latter part may again be regarded as distributed throughout the field with the density

$$-[B^2-16\pi^2(1+I_0)^2]/8\pi$$

at any point. These results are identical with those deduced for the statical case in § 3.

In the case when the magnetisation follows a linear isotropic law the expression for the total energy in the field again reduces to the simple form which expresses it as a distribution with density

$$-(B^2-16\pi^2J_0^2)/8\pi\mu$$

at any place, just as in the previous case.

7. Of the total energy of purely magnetic nature stored up in the field, and of amount

$$= \frac{1}{8\pi} \int dv \{ B^2 - 16\pi^2 (I + I_0)^2 \},$$

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the part

$$-\frac{1}{4\pi}\int dv \int_0^{\rm B} ({\rm H}d{\rm B})$$

is concerned mainly with the currents and is, in fact, the potential function of their mechanical interactions and of the interactions of the magnets with them. A similar transformation, the converse of that applied in § 6, soon shows that this part is equivalent to

$$-\sum_{\ell} \frac{1}{\ell} \int_{0}^{\mathbf{N}} \mathbf{J} d\mathbf{N}.$$

If there is no rigid magnetism about this is the only portion of the total energy in the field that is mechanically available.

Of the rest of the energy the part

$$-\int dv \int_0^{\Pi} (\mathbf{I}_0 d\mathbf{H})$$

is similarly concerned with the rigidly magnetised masses, being, in fact, the force function of their mechanical interactions and the interactions of the field with them.

The remainder, or

$$= \int dv \int_{0}^{\mathbf{H}} (\mathbf{I}d\mathbf{H}),$$

is concerned in a similar way with the induced polarisations.

8. In conclusion we may state that in a general formulation of the energy relations of the magnetic field complete consistency is obtained by using the magnetic induction instead of the magnetic force as the fundamental vector of the theory. This arises partly on account of the main characteristic properties of that vector and partly from the fact that the total energy in the field may be expressed in a form which exhibits it as consisting of the intrinsic energy of the induced polarisations together with an amount equivalent to a distribution with density differing from  $-B^2/8\pi$  by the purely local term  $2\pi(1+I_0)^2$ . This latter part can only represent energy of a purely local or constitutive character and in a mechanical theory would be omitted entirely.

Moreover in this formulation, the total energy in the field when the induction follows a linear law is practically expressible in the form

$$-\frac{1}{8\pi}\int \frac{\mathrm{B}^2}{\mu}\,dv,$$

which is consistent with the value for the density in free either ( $\mu = 1$ ).

It is, perhaps, necessary to emphasise the fact that, throughout the present discussion, magnetic energy is treated as potential energy. If it is desired, as usual, to treat it as kinetic energy, all signs must be reversed. In

general dynamics it is the Lagrangian function L = T-W that determines everything, so that, if a part of the energy is reckoned as kinetic energy, it has the opposite sign to what it would have if reckoned as potential energy. The failure to recognise this difference in the two types of energy in the present instance appears to be the cause of much of the confusion in the subject. The usual treatment of the energy relations of the magnetic field gives the same sign to a quantity which in the statical case is treated as potential energy and in the dynamical case as kinetic energy, and this apparent agreement of sign appears to satisfy most authors, so that the real discrepancy has rarely been noticed. The present mode of treatment has actually been suggested by Cohn,\* but he rejects it as unsatisfactory, because it leads to opposite signs for kinetic and potential energies. In another place Jeans† comes up against the opposite signs, but reconciles them by finding that one of the expressions compared is incomplete by an amount which makes the signs the same.

On Phenomena relating to the Spectra of Hydrogen and Helium. By T. R. Merton, D.Sc., and Prof. J. W. Nicholson, M.A., D.Sc.

(Communicated by A. Fowler, F.R.S. Received June 16, 1916.)

(Abstract.)

In a previous paper the structure of broadened spectrum lines was investigated by a method involving the use of a neutral-tinted wedge as an accessory to the spectroscope. The present communication deals with a method for the accurate determination of the photographic intensities of spectrum lines and the reduction of such intensities to absolute values by comparison with the continuous black-body radiation of the carbon arc.

These methods have been applied to a study of the relative intensity distribution in the spectra of helium and hydrogen under different conditions of excitation.

It has been found that under certain specified conditions there is a transfer of energy from the longer to the shorter wave-lengths in any given series, and that, under such conditions, the associated series, and in particular the Diffuse series, are relatively enhanced at the expense of the Principal series.

<sup>\* &#</sup>x27;Das Electromagnetische,' p. 300.

<sup>† &#</sup>x27;Electricity and Magnetism,' p. 432.

It has also been found that the distribution of intensity found in certain celestial spectra can be approximately reproduced in the laboratory.

In any attempt to interpret the phenomena observed in connection with the Balmer series of hydrogen, it is necessary to know the particular type to which this series belongs. In order to decide this point a study has been made of the separations of the components of lines of the Balmer series of hydrogen, and the mean values of the separations of the doublets constituting the lines  $H_{\alpha}$  and  $H_{\beta}$  have been found to be respectively 0·132 Å.U. and 0·033 Å.U. These values are consistent with the separations appropriate to a Principal series, and the first is in precise agreement with the value deduced by Buisson and Fabry.

These results have been obtained by crossing a Lummer Gehrcke plate with the neutral wedge, and submitting the contours obtained to mathematical analysis, by means of which the distribution of intensity in the individual components, and the separation of the components, can be determined.

On Multiple Integrals.

By Prof. W. H. Young, Sc.D., F.R.S.

(Received July 16, 1916.)

§ 1. In the modern theory of absolutely convergent integrals, as distinct from the older Riemann theory, the difference between multiple and repeated integration falls to the ground. Every multiple integral is equal to the corresponding repeated integrals, and the formulæ involving such multiple integrals, even when expressed without the repeated integral notation, can be obtained by means of the repeated integration process. To really grasp the distinction\* between multiple and repeated integrals we have to take as independent variables functions of bounded variation; more precisely, we have to replace the ensemble of variables (x, y, z, ...) by a single function of bounded variation, which, indeed, takes the place of the product of the variables xyz..., the more general integration reducing to the ordinary when this product replaces the function in question.

I have already had occasion elsewhere to explain what is meant by a function of bounded variation of any number of variables, and to define

<sup>\*</sup> In the French language there is said to be, as yet, no word expressing this distinction.

integration of any bounded function, and absolutely convergent integration of unbounded functions, with regard to such functions of bounded variation. It will be sufficient here to call special attention to the fact that a function of bounded variation, for simplicity, let us say, of two variables, x and y, is expressible, to a value of the function pres, as the difference of two functions, which are monotone increasing in x, in y, and in (x, y), representing the positive and negative variations in the plane, increased by the differences of the variations along the axis of x and along the axis of y respectively. There is, in consequence of the definition, a unique limit at each point for each of the four standard modes of approach, these four limits coinciding, except at points lying on a countable set of lines parallel to the axes at most. The modes of approach here considered correspond to the four quadrants when the point is the origin, the lines corresponding and parallel to the axes being excluded. The limits along these excluded lines may be different from one another and from the other four.\*

Such functions, then, cannot in general be double integrals of ordinary functions of two variables, even if they are continuous. The simplest case, one which constantly occurs in practice, is that in which the functions are not integrals, solely because they are not continuous. This is the case, for instance, with the sum-function of the double Fourier series whose general term is  $\sin mx \sin ny/mn$ , which is discontinuous at the origin and along the axes, and is the simplest type of double integral elsewhere.

The step taken in extending the theory of integration to that in which the ordinary variables are replaced by one or more functions of bounded variation, is for this very reason a matter to which no one who has occasion to use mathematical analysis can be indifferent, though he may be quite unaware of the existence of continuous functions of bounded variation which are not integrals.

The original idea of introducing integration with respect to a monotone function of a single independent variable is due to Stieltjes, and was employed by him exclusively in the case of continuous integrands. Indeed, his definition fails in general with a less restricted hypothesis. On the other hand, Lebesgue has given a definition,† depending on change of the independent variable, for integration of any bounded function with respect to a continuous function of bounded variation. In my own theory, in which the treatment runs precisely parallel to that I have employed when the variable itself is the integrator (that is, the function with respect to which we integrate), the integrand and integrator are both perfectly general, the latter being any function of

<sup>\*</sup> This could only be at the exceptional points already mentioned.

<sup>†</sup> Lebesgue's method fails when there are more independent variables than one.

bounded variation, not necessarily continuous, and the former any bounded or unbounded function to which the process is applicable. In the case in which the integrator is an absolutely convergent integral, we obtain ordinary Lebesgue integrals, and I have utilised this fact on more than one occasion to obtain new theorems in ordinary integration.

In a recent paper, I have thus obtained the generalisation for any number of variables of the second theorem of the mean in Bonnet's and other forms, as well as the formula for integration by parts in its most general form.

In such applications, certain fundamental theorems connecting ordinary integration with the more general type I have here in mind, are necessary. Moreover, in the development of the new theory itself, a new type of theorem is required. Whereas absolutely convergent multiple integration with respect to the product xyz... is always expressible in the form of a repeated integral, this ceases in general to be the case when the integrator is no longer expressible as the product of factors, each involving a single variable only. It becomes important, therefore, to formulate tolerably wide conditions under which such a reduction of difficulty is possible.

In the present communication to the Society, I propose to give a brief account of some of the formulæ, which, from these two different, but closely allied points of view, are fundamental.

I begin by explicitly stating certain underlying facts on which the theory of integration with respect to a function of bounded variation in two or more variables is based.

I have not introduced any discussion of integration with respect to a continuous function which is not of bounded variation. Many of the formulæ might be deduced from those of the present paper in the case when the integrand is a function of bounded variation, but it seems advisable to reserve the discussion of this subject for a separate communication.

I have also thought it unnecessary to give the formulæ for functions of more variables than two.

§ 2. The function g(x, y) with respect to which we integrate is supposed to be any function of bounded variation with respect to (x, y). Every such function is, however, expressible in the form

$$g(x, y) = g(0, 0) + \pi(x, y) - \nu(x, y),$$

where w(x, y) is the sum of the positive variations of g(x, y) with respect to (x, y), to x and to y respectively, each taken in the rectangle (0, 0; x, y), the last two variations being taken along the axes of x and y, and v(x, y) being similarly defined for the negative variations.

From the definition it follows at once that only P(x, y) and N(x, y), the positive variation and negative variation, taken positively, with respect to (x, y), contribute anything to the double integral with respect to g(x, y), so that g(x, y) is virtually expressible as the difference of P(x, y) and N(x, y), that is the difference of two functions, each of which is monotone increasing with respect to (x, y), to x and to y.

It will be convenient, therefore, to avoid repetition, to suppose that in the enunciation of our theorems g(x, y), the function with respect to which we integrate (integrator) is itself such a function (monotonely monotone increasing function). It is clear from what has been said that there will be no loss of generality in adopting such a course, except in cases where some additional special hypothesis is made with respect to the integrator, which does not ipso facto hold for the functions of which g(x, y) is in general the difference.

The condition that g(x, y) is monotonely increasing with respect to (x, y) is expressed as follows:—

$$\left[g(x,y)\right]_{x,y}^{x+h,y+k} \equiv g(x+h,y+k) - g(x,y+k) - g(x+h,y) + g(x,y) \ge 0$$

$$(0 < h, 0 < k), (1)$$

and may be expressed in words by saying that the plane increment round any rectangle whose sides are parallel to the axes is positive, or more precisely by saying that the monotone increase with respect to either of the variables has an increasing rate as the other variable increases.

From these properties it follows that g(x, y) has a unique limit as we approach any particular point from one side or the other along the axes, or in any manner in each of the completely open quadrants. Denoting the former four limits by  $v_1$ ,  $v_2$ ,  $v_3$ ,  $v_4$ , beginning with the horizontal right hand axis, and proceeding round clockwise, and the latter four by  $u_1$ ,  $u_2$ ,  $u_3$ ,  $u_4$ , beginning with the first, or (+, +)-quadrant and proceeding clockwise, we have the inequalities

Hence also, remembering that g(x, y) lies between  $v_2$  and  $v_4$  or  $v_1$  and  $v_3$ , we can show that g(x, y) is continuous with respect to (x, y), except possibly at points lying on a countable set of parallels to the axes of x and y.

- § 3. The last result enables us to prove, as in the theory of functions of a single real variable,  $mutatis\ mutandis$ , that any simple l or u-function of (x, y) can be expressed as the limit of a monotone sequence of simple l or
- \* W. H. Young, "Integration with Respect to a Function of Bounded Variation," Lond. Math. Soc. Proc., Ser. 2, vol. 12, p. 139 (1913).

*u*-functions\* none of whose discontinuities coincide with discontinuities of g(x, y). We have accordingly, as in the original theory, three methods of starting:—

- (1) By defining the integral of a general simple l or u-function f(x, y). This will not be used in the present note.
- (2) By defining the integrals of special simple l and u-functions, whose discontinuities are not discontinuities of g(x, y). The formula is

$$\int_{0,0}^{a_{i},b_{i}} f(x, y) dg(x, y) = \int_{i=1, j=1}^{m-1, n-1} \int_{i,j} \left[ g(x, y) \right]_{a_{i}, k_{j}}^{a_{i+1}, k_{j+1}},$$

that is

$$\int_{0,0}^{a,b} f(x,y) \, dg(x,y) = \sum_{i=1}^{m-1} \sum_{j=1}^{n-1} f_{i,j}(g_{i,j} - g_{i,j+1} - g_{i+1,j} + g_{i+1,j+1}), \quad (2)$$

where the fundamental rectangle (0, 0; a, b) is supposed divided up by lines parallel to the axes, the feet of which on the x-axis have abscisse  $c_1 = 0, c_2, c_3, \ldots, c_m = a$ , and on the y-axis the ordinates  $k_1 = 0, k_2, k_3, \ldots, k_n = b$ , in any convenient way such that all the discontinuities of g(x, y) lie on the dividing lines, none of which coincide with any of the countable set of lines parallel to the axes on which the discontinuities of g(x, y) lie;  $f_i$ , j then denotes the constant value of f(x, y) in the interior of the rectangle whose left-hand bottom corner is  $(c_i, k_j)$ , and  $g_{i,j}$  is the value of g(x, y) at  $(c_i, k_j)$ .

(3) By defining the integrals of continuous functions. The formula is

$$\int_{0,0}^{a,b} f(x,y) \, dg(x,y) = \operatorname{Lt} \sum_{i=1}^{m-1} \sum_{j=1}^{n-1} f(P_{i,j}) (g_{i,j} - g_{i,j+1} - g_{i+1,j} + g_{i+1,j+1}), \quad (3)$$

where  $P_{i,j}$  is any convenient point in the rectangle whose left-hand bottom corner is  $(c_i, k_j)$ , and the rest of the notation has been already explained.

It may be shown that the integrals we obtain are the same, whichever of the three methods we adopt. The definition of the integral of a function which is the limit of a monotone sequence of functions whose integrals have been previously defined is that it is the limit of the integrals of the functions constituting the sequence. The validity of such a definition follows as in one dimension, and we have, as in one-dimensional theory, the theorem that the integral of f(x, y) is at the same time the lower bound of the integrals of l-functions greater than f(x, y) and the upper bound of the integrals of u-functions less than f(x, y).

- § 4. We can now prove certain formulæ for our double integrals with respect to g(x, y). The method of proof will in general consist in proving the
- \* Such functions are constant in the interior of a finite number of rectangles into which the region of integration is divided by lines parallel to the axis.

formulæ from first principles for one or other of our two standard forms (2) and (3) of the preceding article, and then deducing the result by the method of monotone sequences, either by using generalised induction, or by deducing the truth of the formula for l- and u-functions and applying the theorem mentioned at the conclusion of the preceding article.

We begin by establishing the following extremely important result:-

THEOREM.—If y(x, y) is an absolutely convergent integral with respect to (x, y), then

$$\int_{0,0}^{a,b} f(x,y) \, dy(x,y) = \int_{0,0}^{a,b} f(x,y) \, \phi(x,y) \, d(xy), \tag{4}$$

where  $\phi(x, y)$  is any function of which g(x, y) is the integral, for example the function equal to the repeated differential coefficient of g(x, y), wherever this differential coefficient exists, and equal to zero elsewhere.

Since the rectangle (0,0; x,y) is the sum of the rectangles  $(\lambda, \mu; x,y)$  and  $(\lambda, \mu; 0, 0)$  minus the sum of the rectangles  $(\lambda, \mu; 0, y)$  and  $(\lambda, \mu; x, 0)$ , it follows that

$$\int_{0,0}^{a,b} \phi(x,y) \, dx \, dy = \left[ \int_{A,\mu}^{x,y} \phi(x,y) \, dx \, dy \right]_{0,0}^{a,b} = \left[ g(x,y) \right]_{0,0}^{a,b}.$$

If then f(x, y) is a constant, say c, the left-hand side of (4) is by definition equal to  $c \left[ g(x, y) \right]_{0,0}^{a,b}$ , while the right-hand side, being  $c \int_{0,0}^{a,b} \phi(x,y) \, dx dy$ , has as has just been pointed out, the same value. Thus the formula is true when f is a constant.

Again, if f(x, y) is a simple l or u-function of the special type, its integral with respect to g(x, y) is the sum of the finite number of terms, by the formula (2), each of which is the integral of a constant, and therefore, by what has been proved, is equal to the ordinary double integral of that constant multiplied by  $\phi(x, y)$  over the corresponding rectangle. Summing all these terms, the equation (4) follows in this case.

But if the equation (4) holds for each of the members  $f_1(x, y)$ ,  $f_2(x, y)$ ,... of a monotone sequence, it holds for their limiting function f(x, y), since by definition  $\int_{0,0}^{a,b} f(x, y) \, dy(x, y)$  is the limit of  $\int_{0,0}^{a,b} f_n(x, y) \, dy(x, y)$ , and  $\int_{0,0}^{a,b} f(x, y) \, \phi(x, y) \, dx \, dy$  is the limit of  $\int_{0,0}^{a,b} f_n(x, y) \, \phi(x, y) \, dx \, dy$  by a known theorem.

It follows, therefore, that the theorem is true for general simple l and u-functions, as the limits of monotone sequences of these special functions,

<sup>\*</sup> See a forthcoming paper by the author.

and is therefore true for general l and u-functions, as the limits of monotone sequences of simple l and u-functions.

Hence by generalised induction the theorem is true for all functions which can be obtained as the limits of monotone sequences of functions, starting with simple l and u-functions. This proves the truth of the formula (4).

Similarly we may prove the more general theorem:

**THEOREM.**—If G(x, y) is the integral of r(x, y) with respect to s(x, y), where s(x, y) is a function of (x, y) of bounded variation, we have

$$\int_{0,\,0}^{a,\,b} f(x,\,y) \, d\mathbf{G}(x,\,y) = \int_{0,\,0}^{a,\,b} f(x,\,y) \, r(x,\,y) \, ds(x,\,y). \tag{5}$$

We have in fact only to start from the identity

$$\int_{0,0}^{a,b} r(x,y) \, ds(x,y) = \left[ \int_{\lambda,\mu}^{a,b} r(x,y) \, ds(x,y) \right]_{0,0}^{a,b} = \left[ G(x,y) \right]_{0,0}^{a,b},$$

and the argument is otherwise the same as before.

This general theorem, which I have not hitherto stated, even for functions of a single variable, is of very great use in practice, as it enables us to make in a very simple manner certain transformations in our integrals, which would otherwise scarcely occur to the worker.

§ 5. THEOREM.—If the integrand is independent of one of the variables, the integration reduces to integration with respect to a function of the other variable, in accordance with the formula

$$\int_{0.0}^{a,b} f(x) \, dg(x,y) = \int_{0}^{a} \left[ f \, dg \right]_{y=0}^{b} = \int_{0}^{a} f(x) \, d\left( g(x,b) - g(x,0) \right). \tag{6}$$

To prove this, let f(x) be a continuous function. We then have, by (3),

$$\int_{0,0}^{a,b} f(x) dg(x,y) = \operatorname{Lt} \sum_{i=1}^{m-1} \sum_{j=1}^{n-1} f(c_i) (g_{i,j} - g_{i,j+1} - g_{i+1,j} + g_{i+1,j+1})$$

$$= \operatorname{Lt} \sum_{i=1}^{m-1} f(c_i) (g_{i,1} - g_{i,2} - g_{i,n} + g_{i+1,n}) = \int_0^a f(x) \{ dg(x,b) - dg(x,0) \}.$$

Thus the formula is verified in the case considered. Since, therefore, the left-hand and right-hand sides continually reproduce themselves, when we let f(x) describe monotone sequences, first of continuous functions, then of l and u-functions, which are the limits of such sequences, and so on, it follows that the formula holds for all functions f(x) mathematically definable.

This proves the formula, using generalised induction.

If, however, we prefer to use the theorem alluded to at the end of §3, we only use the above method to prove the formula for l and u-functions, and then remark that  $\int_{0,0}^{a,b} f(x) dg(x,y)$  is the upper bound of the integrals of all

u-functions a(x) less than f(x), and  $\int_0^a f(x) (dg(x, b) - dg(x, 0)$ , being the integral of f(x) with respect to g(x, b) - g(x, 0), is the upper bound of the integrals of the functions a(x) with respect to the same function; since the formula (4) holds for a(x) in place of f(x), it therefore holds as it stands.

This proves the formula also. Thus by either method the formula is verified by monotone sequences.

§ 6. Theorem.—If the integrator g(x, y) contains a parameter t, the result  $o_f$  integration with respect to this parameter is given by the following formula:—

$$\int_{0}^{c} dt \int_{0,0}^{a,b} f(x,y) \, dg(x,y,t) = \int_{0,0}^{a,b} f(x,y) \, d\left(\int_{0}^{c} g(x,y,t) \, dt\right), \tag{5}$$

provided only g(x, y, t) possesses an absolutely convergent integral with respect to t.

Suppose first that f(x, y) is a simple l or u-function of the special type, whose discontinuities are different from any of those of g(x, y, t). Then, denoting  $\int_0^c g(x, y, t)$  by G(x, y), we have by (2),

$$\int_{0}^{c} dt \int_{0,0}^{a_{i}b} f(x,y) dg(x,y,t) = \int_{0}^{c} dt \sum_{i=1}^{m-1} \sum_{j=1}^{m-1} f_{i,j}(g_{i,j} - g_{i,j+1} - g_{i+1,j} + g_{i+1,j+1})$$

$$= \sum_{i=1}^{m-1} \sum_{j=1}^{m-1} f_{i,j}(G_{i,j} - G_{i,j+1} - G_{i+1,j} + G_{i+1,j+1})$$

$$= \int_{0}^{a_{i}b} f(x,y) dG(x,y),$$

since G(x, y) is easily seen to be a simple function of the same special type as g(x, y). This proves the formula in this case.

But if  $f_1(x, y)$ ,  $f_2(x, y)$ ,..., are functions forming a monotone sequence with f(x, y) as limit, we may integrate this sequence term-by-term with respect to the function  $\int_0^c g(x, y, t) dt$ , so that

$$\int_{0,0}^{a,b} f(x,y) \, dG(x,y) = Lt \int_{0,0}^{a,b} f_n(x,y) \, dG(x,y).$$

And also similarly

$$\int_{0,0}^{a,b} f(x,y) \, dg(x,y,t) = \underset{n\to\infty}{\text{Lt}} \int_{0,0}^{a,b} f_n(x,y) \, dg(x,y,t).$$

Denoting the function of t represented by either side of the last equation by q(t), and the function whose limit is taken on the right by  $q_n(t)$ ,  $q_n(t)$ 

\* It is convenient here as elsewhere to suppose f positive in the proof. This is no restriction, as we may always break up f into the difference of two such functions.

increases or decreases with n, according as  $f_n(x, y)$  does so, and therefore also describes a monotone sequence with q(t) as limit. Therefore, as before, we may integrate term-by-term and write

$$\int_{0}^{c} q(t) dt = \operatorname{Lt}_{n \to \infty} \int_{0}^{c} q_{n}(t) dt.$$

Now, supposing the equation (5) to hold for each of the functions  $f_n(x, y)$ , we have, with our present notation,

$$\int_{0}^{c} q_{n}(t) dt = \int_{0}^{a, b} f_{n}(x, y) dG(x, y).$$

Proceeding to the limit with n, and using the results just obtained, we get therefore

$$\int_{0}^{c} q(t) dt = \int_{0}^{a,b} f(x,y) dG(x,y),$$

which is identical with (5).

If therefore the equation (5) holds for all the members of any monotone sequence of functions, it holds for the limiting function. Thus, as before, the theorem is true, since it has been shown to hold for simple *l*- and *u*-functions of special type.

THEOREM.—If the integrand contains a parameter t, we may integrate with respect to t inside the integral, that is

$$\int_{0}^{c} dt \int_{0}^{a_{1}, b} f(x, y, t) \, dg(x, y) = \int_{0}^{a_{1}, b} \left( \int_{0}^{c} f(x, y, t) \, dt \right) dg(x, y).$$

The proof of this theorem is mutatis mutantis the same as that in the ordinary theory of absolutely convergent integrals.

§ 7. We have already given in § 5 the simplest case in which integration with respect to a function of bounded variation reduces to ordinary integration. We now prove the following further theorems:—

Theorem.—If F(x, y) is an integral\* with respect to x, then

$$\int_{0,0}^{a,b} \mathbf{F}(x,y) \, dg(x,y) = \int_{y=0}^{b} \left[ \mathbf{F}(x,y) \, dg(x,y) \right]_{x=0}^{a} - \int_{y=0}^{a} dx \int_{y=0}^{b} \frac{d\mathbf{F}}{dx} dg(x,y), \quad (6)$$

where  $d\mathbf{F}/dx$  is any one of the derivates of  $\mathbf{F}(x, y)$  with respect to x. In fact, denoting by f(x, y) the function which is equal to the differential coefficient with respect to x of  $\mathbf{F}(x, y)$  wherever this exists and is finite, and is zero, or has any other convenient values, at the remaining set of values of x of content zero, we have

$$\mathbf{F}(x \ y) = \int_{0}^{x} f(t, y) \, dt + \mathbf{F}(0, y).$$

<sup>\*</sup> Absolutely convergent, or Lebesgue, integral.

Now by the formula (4),

$$\int_{0,0}^{a,b} \mathbf{F}(0,y) \, dy(x,y) = \int_{0}^{b} \mathbf{F}(0,y) (dg(a,y) - dg(0,y)),$$

and 
$$\int_0^a dt \int_{t,0}^{a,b} f(t,y) \, dg(x,y) = \int_0^a dt \int_{y=0}^b f(t,y) \, (dg(a,y) - g(t,y)).$$

But change of order of integration is allowable on each side of the last equation\*; thus

$$\int_{0,0}^{a,b} dg(x,y) \int_{0}^{x} f(t,y) dt = \int_{y=0}^{b} dg(a,y) \int_{0}^{a} f(t,y) dt - \int_{0}^{a} dt \int_{y=0}^{b} f(t,y) dg(t,y),$$

which may be written

$$\int_{0,0}^{a,b} (\mathbf{F}(x,y) - \mathbf{F}(0,y)) \, dg(x,y)$$

$$= \int_{0}^{b} {\{\mathbf{F}(a,y) - \mathbf{F}(0,y)\} \, dg(a,y) - \int_{0}^{a} dx \int_{y=0}^{b} f(x,y) \, dg(x,y)}.$$

Using the expression already given for the integral of F(0, y), this gives

$$\int_{0,0}^{a,b} \mathbf{F}(x,y) \, dg(x,y)$$

$$= \int_{0}^{b} \{ (\mathbf{F}(a,y) \, dg(a,y) - \mathbf{F}(0,y) \, dg(0,y) \} - \int_{0}^{a} dx \int_{0}^{b} f(x,y) \, dg(x,y),$$

which is identical with the formula to be proved.

In the theorem just proved the integration is reduced to repeated integration first with respect to a function of bounded variation of one variable, and then with respect to the other variable. From which we get

**THEOREM.**—If F(x, y) is an integral with respect to x, and G(x, y) is an integral with respect to y, and a function of bounded variation with respect to (x, y), then

$$\int_{0}^{a,b} \mathbf{F}(x,y) dG(x,y) = \int_{0}^{b} \left[ \mathbf{F} \frac{dG}{dy} \right]_{0}^{a} dy - \int_{0}^{a} dx \int_{0}^{b} \frac{d\mathbf{F}}{dx} \frac{dG}{dy} dy.$$

Here we have been able to go still farther; all the integrations employed are ordinary.

Again, without any assumption as to the integrator, we can reduce to ordinary integration when the integrand is a double integral. The theorem, which is an immediate consequence of (4) when the formula for integration by parts for multiple integrals is employed, is as follows:—

<sup>\* &</sup>quot;Integration with respect to a Function of Bounded Variation," § 32, p. 148.

THEOREM.—If f(x, y) is a double integral with respect to (x, y), then  $\int_{0}^{a, b} f(x, y) dg(x, y)$ 

$$= \left[ fg \right]_{0,0}^{a,b} - \left( \int_{x=0}^{a} \left[ \frac{df}{dx} g \right]_{y=0}^{b} dx - \int_{x=0}^{b} \left[ \frac{df}{dy} g \right]_{x=0}^{a} dy + \int_{0,0}^{a,b} \frac{d^{2}f}{dx dy} g dx dy.$$
 (8)

This theorem also follows from (6) by the formula for integration by parts for integration of functions of a single variable.

§ 8. We shall now find it convenient to prove the following property of our integrator g(x, y). This is that the derivates of g(x, y) with respect to either variable are monotone ascending functions of the other variable.

In fact the relation (1) gives

$$\frac{g(x+h,y+k) - g(x+h,y)}{k} \ge \frac{g(x,y+k) - g(x,y)}{k} (0 < h; 0 < k).$$

Let k describe such a sequence of positive values with zero as limit that the right-hand side approaches its upper limit, the upper right-hand derivate of g(x, y) with respect to y, say  $g_{(y)}^+(x, y)$ . Then the left-hand side approaches some limit or limits which are not greater than  $g_{(y)}^+(x+h, y)$ . Thus

$$g_{(y)}^+(x+h, y) \ge g_{(y)}^+(x, y).$$

Similarly, choosing the sequence of values of k so that the left-hand side approaches its lower limit  $g_{+}^{(y)}(x+h, y)$ , the lower right-hand derivate of g with respect to y, we get

$$g_{+}^{(y)}(x+h, y) \succeq g_{+}^{(y)}(x, y).$$

This shows that both the right-hand derivates of g(x, y) with respect to y are monotone ascending functions of x. Similarly, taking h positive and k negative, in which case the symbol  $\geq$  in (1) must, of course, be changed to  $\leq$ , in order that the plane increment may begin with the right-hand top corner, and proceed clockwise, we find that both the left-hand derivates of g(x, y) with respect to y are monotone ascending functions of x.

By symmetry the same result holds when x and y are interchanged. This, therefore, proves the required result.

§ 9. If g(x, y), in addition to having the property of being what we have called a monotonely monotone function of (x, y), (§ 2), is an integral with respect to x, it is the integral of any one of its derivates with respect to x. These derivates agree and are finite except at a set of content zero of values of x for each fixed value of y and, therefore, agree and are finite except at a set of values of (x, y) of plane content zero. Hence they agree and are finite except at a set of content zero of values of x fixed value of x not belonging to a certain set of content zero of values of x. Putting aside this exceptional

set of values of x, therefore, it follows from §8 that, x being constant, dg/dx exists and is finite except at a set of content zero of values of y, and the values at the exceptional points may be so assigned that dg/dx becomes a monotone ascending function of y, defined for all values of y.\* With this understanding therefore we may, when g(x, y) is an integral with respect to x, not only write  $g(x, y) = \int (dg/dx) dx$ , but also we may integrate a function with respect to dg/dx, x being constant, and then integrate the result with respect to x, the exceptional set of content zero of values of x at which the inside integral is undefined not affecting the second integration.

With this understanding, we have the following theorem on the reduction to a repeated integral:—

THEOREM.—If y(x, y) is a monotonely monotone ascending function of (x, y) and an integral with respect to x, and therefore an integral with respect to x of a monotone increasing function of y, we may write

$$\int_{0}^{a,b} f(x,y) \, dg(x,y) = \int_{0}^{a} dx \int_{0}^{b} f(x,y) \, d(dg/dx). \tag{7}$$

If f(x, y) is a constant, say c, the theorem is at once seen to be true, for, by definition, the left-hand side of the equation is

$$c(g(a, b)-g(a, 0)-g(0, b)+g(0, 0)),$$

and the right-hand side is the same, since, performing the inside integration, we get, writing g'(x, y) for dg/dx,

$$\int_{0}^{a} c(g'(x, b) - g'(x, 0)) dx.$$

Hence, by the formula (2), the theorem holds when f(x, y) is a simple l- or u-function of the special type, for the integral is then a double summation of a finite number of such integrals with constant integrands.

But any simple l- or u-functions can be expressed as the limit of a monotone sequence of simple function of the special types just contemplated, say,

$$f_1(x, y) \leq f_2(x, y) \leq \ldots \rightarrow f(x, y),$$

and we may integrate this sequence term-by-term either with respect to g(x, y), or first with respect to g'(x, y), x being constant, and then with respect to x.

Thus 
$$\int_{0,0}^{a,b} f(x,y) \, dg(x,y) = \underset{n \to \infty}{\text{Lt}} \int_{0,0}^{a,b} f_n(x,y) \, dg(x,y),$$
 and also 
$$\int_{0}^{a} dx \int_{0}^{b} f(x,y) \, dg'(x,y) = \underset{n \to \infty}{\text{Lt}} \int_{0}^{a} dx \int_{0}^{b} f_n(x,y) \, dg'(x,y).$$

\* This mode of regarding the matter is sufficient for the purpose of justifying the notation dg/dx in equation (7). For fuller information with regard to the derivates and repeated derivates of functions of bounded variation, see the forthcoming paper referred to in §4.

But, by what we have already proved,

$$\int_{0}^{a,b} f_{n}(x,y) \, dg(x,y) = \int_{0}^{a} dx \int_{0}^{b} f_{n}(x,y) \, dg'(x,y).$$

From these three relations the required relation immediately follows.

Similarly, it now follows generally for any l- and u-functions, these being the limits of monotone sequences of simple l- and u- functions.

But this proves the theorem generally by generalised induction, or, if we prefer, as follows: the left-hand side of (7) is the upper bound of  $\int_{0,0}^{a,b} \phi(x,y) \, dy(x,y)$ , where  $\phi(x,y)$  is any *u*-function less than f(x,y); and the right-hand side of (7) is the integral with respect to x of the upper bound of  $\int_{0}^{b} \phi(x,y) \, dy'(x,y)$ , which is the same as the upper bound of  $\int_{0}^{a} dx \int_{0}^{b} \phi(x,y) \, dy'(x,y)$ .

For  $\int_0^b \phi \, dg' = \int_0^a f \, dg'$ , so that integrating, with respect to x, and taking the upper bound, the upper bound of  $\int_0^a dx \int_0^b \phi \, dg' = \int_0^a dx \int_0^b f \, dg'$ . But we can find a  $\phi$  for which  $\int_0^b \phi \, dg'$  differs by as little as we please from  $\int_0^b f \, dg'$ , so that integrating with respect to x and taking the upper bound, we see that the upper bound of  $\int_0^a dx \int_0^b \phi \, dg' \ge \int_0^a dx \int_0^b f \, dg' - ea$ , where e is as small as we please. From this the truth of the statement made at once follows.

But by what has been proved

$$\int_{0,0}^{a,b} \phi(x,y) \, dg(x,y) = \int_{0}^{a} dx \int_{0}^{b} \phi(x,y) \, dy'(x,y),$$

so that the upper bounds of the two sides of this equation are also equal. This gives us the equation (7), and proves the theorem.

§ 10. From the theorem of the preceding article, we at once deduce the following:—

THEOREM.—If g(x, y) is a monotonely monotone ascending function of (x, y), and an integral with respect to x, and therefore an integral with respect to x of a monotone increasing function of y, we have

$$\frac{d}{dx}\int_{0,0}^{x,y}f(u,v)\,dg(u,v) = \int_{0}^{y}f(x,v)\,d\left(\frac{dg(x,v)}{dx}\right),\tag{8}$$

provided the right-hand side is a continuous function of x.

§ 11. When the integrator, instead of the integrand, describes a sequence, the mere monotony of the sequence is not enough to ensure that the limiting process is allowable, that is, that the integral with respect to the limit is the same as the limit of the integral.

In this connection the following theorem is of importance:-

**THEOREM.**—If g(x, y, z) is a function of (x, y), which is monotonely increasing with respect to x, to y, and to (x, y), and has its triple increment always of the same sign, while it is monotone with respect to z, then

$$\operatorname{Lt}_{z \to c+0} \int_{0,0}^{a,b} f(x,y) \, dg(x,y,z) = \int_{0,0}^{a,b} f(x,y) \, dg(x,y,c+0).$$
 (9)

From the hypothesis in the enunciation it follows that

$$g(x, y, c+k)-g(x, y, c+0),$$
 (0 < k),

is monotonely monotone increasing with respect to (x, y), supposing the triple increment of g to be positive. For the function here considered is the limit, as  $e \to 0$  through positive values, of

$$g(x, y, c+k)-g(x, y, c+e),$$
  $(c < k)$ 

which is monotonely monotone increasing with respect to (x, y).

Hence if f(x, y) is a bounded function of (x, y), and is numerically  $\leq M$ ,

$$\left| \int_{0,0}^{a,b} f(x,y) d(g(x,y,c+k) - g(x,y,c+0)) \right| \\ \leq \mathbf{M} \left[ g(x,y,c+k) - g(x,y,c+0) \right]_{0,0}^{a,b}.$$

and hence has the unique limit zero as  $k \to 0$ . This proves the theorem when f(x, y) is bounded.

When f(x, y) is not bounded, we denote by  $f_m(x, y)$  the function which is equal to f, where this is less than m, and is elsewhere equal to m (f being as usual taken to be positive). Making then  $m \to \infty$ , we see, by monotone sequences, that the theorem is true.

As a particular case of the theorem just proved, we have the following:—
THEOREM.—If  $g_n(x, y)$  is a monotonely monotone increasing function of (x, y), and has, as  $n \to \infty$ , g(x, y) as limit, and generates such a monotone increasing or decreasing sequence that its double increment always increases, or always decreases, with n, then

$$\underset{n\to\infty}{\text{Lt}} \int_{0,\,0}^{a,\,b} f(x,\,y) \, dg_n(x,\,y) = \int_{0,\,0}^{a,\,b} f(x,\,y) \, dg(x,\,y).^*$$
 (10)

\* This theorem may be utilised, among other ways, in extending the theorem of Integration by Parts.

# On the Order of Magnitude of the Coefficients of a Fourier Series. By Prof. W. H. Young, Sc.D., F.R.S.

## (Received August 9, 1916.)

§ 1. Riemann's theorem that the coefficients of a Fourier series converge to zero was shown by Lebesgue to still hold when integration is understood to be in the general sense now employed, absolutely convergent, or Lebesgue integration. Little progress has, however, been made in the determination of the order of magnitude of the coefficients. It has, indeed, been proved that, when the function has bounded variation,  $na_n$  and  $nb_n$  are bounded functions of n, and that, when the function is a continuous function of such a type as satisfies a condition of Lipschitz,\*  $n^ga_n$  and  $n^gb_n$  converge to zero, where q is a positive number not greater than unity, depending on the particular Lipschitz condition satisfied by the function. As regards the second of these results, involving the satisfying of a condition of Lipschitz, it is to be remarked that, in well-known series of the type

$$\sum n^{-q} \cos nx$$
 and  $\sum n^{-q} \sin nx$ ,

the functions of which they are the Fourier series do not, in any interval containing the origin, satisfy any condition of Lipschitz, being, indeed, unbounded.

In the present communication I obtain a number of theorems corresponding to each of these two results, including them as particular cases, and, at the same time, leading to the known properties of the simple sine and cosine series above referred to.

It will be remarked that the conditions supposed to hold in the neighbourhood of the origin and the remaining part of the interval of periodicity are different; this is inevitable, if they are to be as wide as possible. It might be, perhaps, supposed a priori that conditions of a far more general type would be adequate; this is not, however, the case. It is still more unusual for  $na_n$  and  $nb_n$  to converge than it is for the Fourier series to converge. Indeed, if the Fourier series converges at the origin, and  $na_n$  converges to zero, the Fourier series must do more than ordinarily converge, it must converge to a Cesàro order of negative unity. A similar statement holds good of the convergence of  $a_n$  and  $b_n$  when multiplied by a function of n of lower order of magnitude than n. There is, however, a

<sup>\*</sup> H. Lebesgue, "Sur la représentation trigonométrique approchée des fonctions satisfaisant à une condition de Lipschitz," 'Bull. de la Soc. Math. de France,' vol. 38, pp. 1-27 (1910).

theory of Cesaro convergence of successions analogous to that for series, where we consider instead of the convergence of  $na_n$ ,  $nb_n$ ,  $n^aa_n$ ,  $n^ab_n$ , the arithmetical integral, or fractional, means of these quantities.

When this is done, more general results are possible. For example, if the Cesàro order is of a type greater than or equal to unity, only the nature of the function in a small neighbourhood of the origin matters, equally when we consider convergence or oscillation.

We can, however, no longer, in employing this theory, speak of the results obtained as referring to the order of magnitude of the coefficients of a Fourier series. I propose, however, as they have an important application in the theory of Fourier series, to consider these questions on a subsequent occasion.

For simplicity of expression, the theorems have been stated for functions which are either odd or even. It is hardly necessary to point out that the results are perfectly general; when f(x) is not itself odd or even,  $\frac{1}{2}[f(x)+f(-x)]$  is the even, and  $\frac{1}{2}[f(x)-f(-x)]$  the odd, function which takes the place of f(x) in the theorems,  $a_n$  and  $b_n$  being then the coefficients of  $\cos nx$  and  $\sin nx$  in the Fourier series of f(x).

§ 2. For completeness the theorem about to be given and the following one are stated generally, though information as to the order of the coefficients  $a_n$  and  $b_n$  is only given by the latter half of each.\*

THEOREM 1.—If an be the typical coefficient of the Fourier series of an even function of bounded variation, then

$$na_{-} \neq 0$$
.

when the convergence is taken in the Cesàro manner, of any positive type whatever; moreover, the convergence is ordinary convergence if the function be an integral in every interval not containing the origin.

Let g(x) be the function in question, then

$$na_n = \frac{1}{\pi} \int_{-\pi}^{\pi} ng(x) \cos nx \, dx = \frac{2}{\pi} \int_{0}^{\pi} g(x) \, d(\sin nx) = -\frac{2}{\pi} \int_{0}^{\pi} \sin nx \, dg(x)$$
$$= -\frac{2}{\pi} \int_{0}^{\pi} \sin nx \, dg(x) - \frac{2}{\pi} \int_{0}^{c} \sin nx \, dg(x).$$

Case 1. Let g(x) be an integral in every interval not containing the origin; then by the Theorem of Riemann-Lebesgue the first term of the expression just written down approaches zero.

\* It should be remarked that the second half of Theorem 1, if we assume the known properties of a function of bounded variation, reduces to the theorem which I have called that of Riemann-Labesgue. It is inserted to preserve the parallelism between the Fourier series and its allied series. The whole of Theorem 2 breaks new ground.

Case 2. If g(x) be not such an integral, then the first term approaches zero, when the convergence is taken in the Cesaro manner, with any positive index, as is easily seen,\* but does not do so in the ordinary manner.

In either case we reduce to the consideration of the second term. This is numerically  $\leq \frac{2}{\pi} \int_0^c \left| dg(x) \right|$ ; and therefore is as small as we please, if g(x) is continuous at the origin.

But even if y(x) is discontinuous at the origin, such a discontinuity could not affect this fact, since  $\sin nx$  is zero at the origin. Therefore in all cases the second term in our expression approaches zero, which proves the theorem.

THEOREM 2.—If  $b_n$  be the typical coefficient of the Fourier series of an odd function of bounded variation, then

$$nb_n \rightarrow \frac{1}{\pi}(g(+0)-g(-0)) = \frac{1}{\pi}(jump \ at \ the \ origin),$$

when the convergence is taken in the Cesàro manner, of any positive type whatever; moreover, the convergence is ordinary convergence if the function be an integral in every interval not containing the origin.

Let g(x) be the odd function of bounded variation. Its Fourier series is unaffected by the values of g(x) at the origin and the extremities  $\pi$  and  $-\pi$ , and we may therefore with advantage suppose the value of g(x) at these points to be that given by summing the Fourier series of g(x), namely zero, so that

$$g(0) = g(\pi) = g(-\pi) = 0.$$

We then have, if  $b_n$  be the typical Fourier coefficient of g(x),

$$nb_{n} = \frac{1}{\pi} \int_{-\pi}^{\pi} ng(x) \sin nx \, dx = \frac{1}{\pi} \int_{0}^{\pi} n(g(x) - g(-x)) \sin nx \, dx$$

$$= -\frac{2}{\pi} \int_{0}^{\pi} g(x) \, d(\cos nx) = \frac{2}{\pi} \int_{0}^{\pi} \cos nx \, dg(x)$$

$$= \frac{2}{\pi} \int_{0}^{\pi} \cos nx \, dg(x) + \frac{2}{\pi} \int_{0}^{\pi} \cos nx \, dg(x).$$

Case 1. Let g(x) be an integral in every interval not containing the origin; then the first term in the expression just obtained approaches zero as  $n \to \infty$ , by the Theorem of Riemann-Lebesgue.

\* In fact  $\sum \sin nx$  oscillates boundedly for  $e \le x \le \pi$ , and therefore  $\frac{1}{n^k} \sum_{1}^{n} \sin nx \to 0$  boundedly when k > 0. It follows that  $\sum_{1}^{n} \sin nx \to 0$  boundedly, if summed in the Cesaro manner, index k. This bounded sequence can by a known theorem be then integrated with respect to g(x) term-by-term.

Case 2. Let g(x) not be such an integral, then the first term approaches zero, as  $n \to \infty$ , provided the convergence be taken in any Cesàro manner, index > 0.\* Thus only the second term needs consideration. But this differs from  $2g(+0)/\pi$  by a quantity which is numerically  $\leq 2(V(e)-V(+0))/\pi$ , where V(x) is the total variation of g(x), by a quantity which is as small as we please, e being chosen sufficiently small. Thus

$$nb_n = 2g(+0)/\pi = (g(+0)-g(+0))/\pi = \frac{1}{\pi}(jump \text{ at the origin}),$$

the convergence being in the Cesàro or ordinary manner, according as we have to do with Case 1 or Case 2. This proves the theorem.

§4. The former of the two preceding theorems enables us to prove immediately that the derived series of the Fourier series of a function of bounded variation converges (C, k-1), (0>k); more generally it converges with any negative Cesàro type on the positive side of -1. The latter of our theorems gives us the corresponding theorem for the convergence of the allied series, involving the usual further condition.† The two theorems also show that, when g(x) is an integral in every interval not containing the origin, the convergence is (C, -1).

In the second half of Theorems 1 and 2<sup>+</sup> we may, both in the enunciation and in the proof, avoid the concept of function of bounded variation by changing the condition that the function should have bounded variation into what is in our case the equivalent condition that the differential coefficient of the function should possess an absolutely convergent integral.

We divide the interval (0, e) at the point  $2\pi/n$ . We then have

$$\int_{0}^{2\pi/n} f(x) \, n \, \frac{\cos}{\sin} \, nx \, dx = \int_{0}^{2\pi} f(x/n) \, \frac{\cos}{\sin} \, x \, dx + \int_{0}^{2\pi} f(+0) \, \frac{\cos}{\sin} \, x \, dx + 0,$$

since, for all points x of the completely open interval  $(0, \pi)$ 

$$f(\boldsymbol{\pi}) - f(x) = \int_{x}^{\boldsymbol{\pi}} f'(x) \, dx,$$

f(x) being by hypothesis an integral. Indeed the right-hand side having by hypothesis a unique finite limit when  $x \to 0$ , the same is true of the left-

<sup>\*</sup> This follows from the fact that  $\sum \cos nx$  oscillates boundedly for  $e \le x \le \pi$ , and the rest of the argument is the same as for Theorem 1.

<sup>†</sup> See a forthcoming paper by the author. Cesàro summability of negative integral indices has apparently been regarded as offering difficulties of at least an inconvenient character. In the theory of Fourier series this concept seems to me to be as indispensable as that of ordinary convergence.

<sup>‡</sup> So far as they relate to ordinary convergence of  $na_n$  and  $nb_n$ .

hand side, thus f(+0) exists and is finite. Also by the same equation f(x) approaches this limit boundedly, since the right-hand side is numerically

$$\leq \int_0^{\pi} \left| f'(x) \right| dx.$$

Again

$$\int_{2\pi/n}^{e} f(x) n \frac{\cos}{\sin} nx \, dx = \left[ f(x) \frac{\sin}{1 - \cos} nx \right]_{2\pi/n}^{e} - \int_{2\pi/n}^{e} f' \frac{\sin}{1 - \cos} nx \, dx,$$

where the last integral is numerically

$$\leq \int_0^\varepsilon \left| f'(x) \right| dx,$$

which is as small as we please, c being chosen conveniently small.

Hence, as before, the required results at once follow.

§ 5. In the next two theorems the assumptions made render f(x) an absolutely convergent integral in every interval not containing the origin. The following simple lemma is used in the proofs.

**Lemma.**—If f(x) is an absolutely convergent integral in the interval  $(e, \pi)$ , where 0 < e, then

$$\lim_{n\to\infty} \left\{ \int_e^{\pi} f(x) n \cos nx + f(ne) \sin ne \right\} = 0$$

and

$$\lim_{n\to\infty}\left\{\int_{\ell}^{\pi}f(x)\,n\,\sin\,nx-f(n\ell)\cos\,ne\right\}\,=\,0,$$

provided in the latter case  $f(\pi) = 0$ , e.g., if f(x) is an odd function represented at  $x = \pi$  by its Fourier series.

We have in fact only to integrate by parts, and use the Theorem of Riemann-Lebesgue, by which  $\int_{cos}^{\pi} f'(x) \frac{sin}{cos} ux \, dx$  has the limit zero.

We now have the following theorem:—

THEOREM 3.—If f(x) is an even function, which in a certain neighbourhood (-e, e) surrounding the origin is such that  $x\frac{df}{dx}$  is a function of bounded variation, and in the remaining part of the interval  $(-\pi, \pi)$  is itself an absolutely convergent integral, then the coefficients of the derived series of the Fourier series of f(x) converge to a unique limit, namely  $\lim_{x\to 0} \left(-x\frac{df}{dx}\right)$ .

If  $a_n$  is the typical Fourier coefficient of f(x), we have

$$\frac{1}{2}\pi na_n = \int_0^\pi f(x) n\cos nx \, dx = \underset{t\to 0}{\text{Lt}} \int_t^\pi f(x) n\cos nx \, dx + \int_t^\pi f(x) n\cos nx \, dx$$

$$= \int_t^\pi f(x) n\cos nx + f(ne)\sin ne - \underset{t\to 0}{\text{Lt}} \left( f(t)\sin nt + \int_t^\pi f'(t)\sin nt \, dt \right), \quad (1)$$

since f(t) is the integral of f'(t), in the interval (t, e), for in this interval, not containing the origin, f'(t) is bounded.

Now if we write g(x) for xf'(x), we have

$$\left| f(e) - f(t) \right| = \left| \int_{t}^{e} f'(t) dt \right| = \left| \int_{t}^{e} \frac{g(t)}{t} dt \right| \le A \left( \log r - \log t \right).$$

where A is the upper bound of [g(x)] in (0, e). Therefore t f(t) certainly approaches zero as t approaches zero, and therefore the same is true of  $f(t) \sin nt$ , n being for the moment fixed. Thus the limit on the right of (1) reduces to  $\int_{a}^{c} f'(t) \sin nt dt$ .

Using the Lemma ( $\S 5$ ), we have therefore, by (1).\*\*

$$\operatorname{Lt}_{n\to\infty} \frac{1}{2}\pi na_n = -\operatorname{Lt}_{n\to\infty} \int_0^x xf'(x) \frac{\sin nx}{x} dx = -\operatorname{Lt}_{n\to\infty} \int_0^x g(x) \frac{\sin nx}{x} dx \\
= -\operatorname{Lt}_{n\to\infty} \int_0^x g(x) n \phi'(nx) dx. \quad (2)$$

where

$$\phi(t) = \int_0^t \frac{\sin t}{t} dt,$$

and is therefore a bounded function of t in the whole infinite interval  $(0, \infty)$ . Now  $\phi(x)$  being an absolutely convergent integral in any finite interval, and g(x) a function of bounded variation, we may integrate by parts and write

$$\underset{n\to\infty}{\text{Lt}} \frac{1}{2}\pi na_n = \underset{n\to\infty}{\text{Lt}} \left\{ -g(e)\phi(ne) + \int_0^c \phi(nx) \, dy(x) \right\}.$$

But as  $n\to\infty$ ,  $\phi(nx)\to \frac{1}{2}\pi$ , except at x=0, where its value remains zero, and the approach of  $\phi(nx)$  to its limit is bounded. Thus by a known theorem in the theory of integration with respect to a function of bounded variation.

Lt 
$$\frac{1}{2}\pi na_n = -y(e)\frac{1}{2}\pi + \text{Lt}\int_0^e \phi(nx)\,dy(x)$$
  

$$= -g(e)\frac{1}{2}\pi + \int_{+0}^e \frac{1}{2}\pi\,dy(x) + \int_0^{+0} dy(x) = \frac{1}{2}\pi\,y(+0);$$
thus
$$\text{Lt } na_n = y(+0).$$

which proves the theorem.

COR.—If f(x) is an even function, such that x(df/dx) is a function of bounded variation throughout the whole interval  $(-\pi, \pi)$ , then the theorem is true.

<sup>\*</sup> The integrals in (2) are Lebesgue integrals, since g(x) has an absolutely convergent integral from 0 to e, and  $\sin nx/x$  is continuous.

§ 7. It will be noticed that, from and after the equation (2), in which the absolutely convergent integral  $\frac{1}{\pi} \int_0^t g(x) \frac{\sin nx}{x} dx$  occurs, the proof consists merely in proving that this has the unique limit g(+)0. Neglecting quantities which vanish when n increases indefinitely, this is the expression for the sum of n terms of the Fourier series of g(x); we might, therefore, have simply quoted Dirichlet's results here, and omitted the rest of the proof. I preferred, however, to give what is virtually a new proof of this theorem of Dirichlet's.

The proof of the following theorem has been written out slightly differently from that of the preceding theorem. Had we pursued the same lines,  $(1-\cos nx)$  would have taken the place of  $\sin nx$  in the preceding article, in this sense, that we should have reduced the discussion to that of the absolutely convergent integral  $\frac{1}{\pi} \int_0^s g(x) \frac{1-\cos nx}{x} dx$ , and accordingly have proved that  $nb_n$  is effectively the sum of the first n terms of the allied series of the Fourier series of g(x). We have, accordingly, in the course of the following proof shown incidentally that the allied series of a function g(x) of bounded variation converges to  $\frac{1}{\pi} \mathop{\rm Lt}_{\epsilon \to 0} \int_{\epsilon}^{\pi} \frac{g(x)}{x} dx$ , provided only this limit exists. This result had already been obtained by me by another method.\*

§ 8. Analogous to the theorem of §6, we have the following:—

THEOREM 4.—If f(x) is an odd function having a definite limit as  $x \to 0$ , and such that, in a certain neighbourhood (-e, e) surrounding the origin, x(df/dx) is a function of bounded variation, while in the remaining part of the interval  $(-\pi, \pi)$ , f(x) is itself an absolutely convergent integral, then the coefficients of the derived series of the Fourier series of f'(x) converge to a unique limit, namely,

$$\underset{n\to\infty}{\text{Lt}} (nb_n) = \frac{1}{\pi} [f(+0) - f(-0)].$$

In fact, writing K for  $2 k\pi/n$ , where k, like n, is an integer,

$$\frac{1}{2}\pi nb_n = \int_0^{\pi} f(x) n \sin nx \, dx = \int_0^K f(x) n \sin nx \, dx + \int_K^{\pi} f(x) n \sin nx \, dx, \quad (1)$$

and

$$\int_{0}^{K} f(x) n \sin nx \, dx = \int_{0}^{2k\pi} f(t/n) \sin t \, dt + \int_{0}^{2k\pi} f(+0) \sin x \, dx + 0. \tag{2}$$

<sup>\* &</sup>quot;Konvergenzbedingungen für die verwandte Reihe einer Fourierschen Reihe," Münchener Bericht, June 10, 1911.

Also

$$\int_{K}^{\pi} f(x) n \sin nx \, dx$$

$$= \int_{a}^{\pi} f(x) n \sin nx \, dx + \int_{K}^{a} f(x) \, d (1 - \cos nx),$$

$$= \int_{a}^{\pi} f(x) n \sin nx \, dx + \left[ f(x) (1 - \cos nx) \right]_{K}^{a} - \int_{K}^{a} x f'(x) \frac{1 - \cos nx}{x} \, dx,$$

$$= \left\{ \int_{a}^{\pi} f(x) n \sin nx \, dx - f(e) \cos ne \right\} + f(K) + \int_{a}^{e} g(x) \frac{\cos nx}{x} \, dx, \quad (3)$$

since f(x) is the integral of f'(x), in the interval (K, e) not containing the origin, for in this interval f'(x) is bounded. Here

$$g\left(x\right) = xf'\left(x\right)$$

is a function of bounded variation. Putting

$$\phi(t) = \int_{2k\pi}^{t} \frac{\cos t}{t} dt,$$

so that  $\phi_i(t)$  is an integral, we may therefore integrate the last term of (3) by parts, and write

$$\int_{\mathbf{K}}^{c} g(x) \frac{\cos nx}{c} dx = \left[ g(x) \phi(nx) \right]_{\mathbf{K}}^{c} - \int_{\mathbf{K}}^{c} \phi(nx) dg(x).$$

This is numerically  $\leq \frac{1}{k\pi} \left( \left| g(e) \right| + \int_{K}^{e} \left| dg(x) \right| \right) \leq \frac{1}{k\pi} 2V$ , where V is the total variation of g(x) from 0 to e, and may therefore be put = M/k, where  $|M| \leq 2V/\pi$ .

Hence, using the Lemma (§ 5), the right-hand side of (3) differs from f(K) + M/k by a quantity which vanishes when  $n \to \infty$ , and differs therefore from f(+0) + M/k by a quantity which vanishes when  $n \to \infty$ . Thus by (1). (2), and (3).

$$\frac{1}{2}\pi nb_n - f(+0)$$

remains, as  $n \to \infty$ , numerically  $\leq 2 V/\pi k$ . But k may be chosen as large as we please, therefore,  $\frac{1}{2} \pi n b_n - f(+0)$  can have no other limit except zero, when  $n \to \infty$ . This proves the theorem.

§ 9. Always provided that we ensure the vanishing in the limit of the portion of our expression due to the interval  $(e, \pi)$  in the Theorems 3 and 4, the problem of the order of magnitude thus reduces to that of determining the conditions of convergence of the Fourier series of  $w df/dx^*$  and of its allied series. Corresponding to every known theorem regarding the convergence

\* This function must accordingly possess an absolutely convergent integral in  $(-\pi, \pi)$ . It will be immediately recognised that this is the case in the theorems given below.

of such series, we have accordingly theorems relating to the order of magnitude of  $na_n$  and  $nb_n$ .

With regard to the coefficient  $b_n$ , it should be remarked that the extra condition for the convergence of the allied series, namely, the existence of the limit of a certain integral, reduces in the case of the order of magnitude problems to the condition that f(x) should have a unique limit as  $x \to 0$ .

Thus we have the following theorems which correspond to a test due to de la Vallée Poussin for the Fourier series, and my counterpart of it for the allied series.

**THEOREM** 5.—If f(x) is an even function, and such that in a certain neighbourhood surrounding the origin

$$\frac{1}{x} \int_{0}^{x} x \, \frac{df}{dx} \, dx$$

is a function of bounded variation, while in every interval not containing the origin f(x) is itself an absolutely convergent integral, then

Lt 
$$na_{n} = \text{Lt}_{x\to 0} \left(-\frac{1}{x} \int_{0}^{c} x \frac{df}{dx} dx\right).$$

**THEOREM 6.—If** f(x) is an odd function satisfying the same conditions, and the further condition that f(+0) exists, then

$$\text{Lt } nb_n = \frac{1}{\pi} (f(+0) - f(-0)).$$

Again, corresponding to tests due to myself, which I have recently simplified, we have the theorems:

Theorem 7.—If f(x) is an even function, and such that in a certain neighbourhood surrounding the origin

$$x\frac{dy}{dx} = \frac{1}{x} \int_0^x h(x) \, dx,$$

where  $\frac{1}{x}\int_0^x |h(x)| dx$  is bounded, while in the remaining part of the interval  $(-\pi, \pi)$ , f(x) is itself an absolutely convergent integral, then

$$\underset{n\to\infty}{\operatorname{Lt}} na_{n} = \underset{x\to 0}{\operatorname{Lt}} \left( -x \frac{df}{dx} \right),$$

this limit being supposed to exist.

THEOREM 8.—If f(x) is an odd function, satisfying the same conditions as in Theorem 7, and satisfying the further condition that f(+0) exists, then

Lt 
$$nb_n = \frac{1}{\pi} [f(+0) - f(-0)].$$

The conditions of Theorems 7 and 8 evidently render f(x) an absolutely convergent integral in every interval not containing the origin. Thus all that is necessary to ensure that the argument employed in Theorems 3 and 4, and explained in § 7, is applicable is to show that, in all the theorems of the present article, xf(x) converges to zero as  $x \to 0$ .

In the cases of Theorems 5 and 6 we have

$$\int_{t}^{e} x \frac{df}{dx} dx = ef(e) - tf(t) - \int_{t}^{e} f(x) dx$$

and therefore, since x df/dx and f(x) are both summable in the whole interval (0, e), by hypothesis, tf(t) has a unique finite limit as  $t \to 0$ . Now this limit cannot be other than zero, for if it were, f(x) would in the neighbourhood of the origin be of the order A/t, and therefore not summable from 0 to e, whereas the Fourier series considered is that of f(x), which is accordingly summable from  $-\pi$  to  $\pi$ .

In the cases of Theorems 7 and 8, x df/dx is bounded and therefore possesses an absolutely convergent integral in  $(0, \epsilon)$ . Also from the identity

$$\frac{d}{dx}[xf(x)] = f(x) + x \, df/dx,$$

we deduce

$$ef(c)-tf(t)=\int_{t}^{c}f(\boldsymbol{x})\,dx+\int_{t}^{c}x\frac{df}{d\boldsymbol{x}}\,dx,$$

since xf(x) is an integral in (t, e). But each of the integrals on the right exists in the whole interval (0, e), therefore the right-hand side of the last equation has a unique finite limit as  $t \to 0$ ; hence also tf(t) has a unique limit, which, as before, must be zero.

§ 10. It will be noticed that, in the next theorems, bounded functions have taken the place of the functions of bounded variation in Theorems 3 and 4. That we could not formerly make this more general assumption is due to the fact that there is a sudden change as p reaches zero when decreasing from unity. Otherwise the two theorems which follow are precisely analogous to Theorems 3 and 4, and constitute, like them, very wide generalisations of the properties of the familiar simple series of cosines or sines.

It should also be remarked that in this and in the following theorems up to Theorem 12, we write the generalised condition of Lipschitz briefly. The notation  $O(h^{1-p})$  must be interpreted to mean

$$\lambda h^{1-p}$$
,  $(0 < \lambda; 0 < p < 1)$ 

 $\lambda$  being a quantity which has finite bounds independent of x and h.

When  $\lambda$  is a quantity as small as we please, which occurs, for example, if the quantity p employed is not the smallest at our disposal (e.g., when there is no smallest), we use o in place of O.

THEOREM 9.—If f(x) is an even function which in a certain neighbourhood (-e, e) surrounding the origin is such that  $x^{1+p} df/dx$  is a bounded function with a unique limit as  $x \to 0$ , and in the remaining part of the interval  $(-\pi, \pi)$  itself satisfies the condition of Lipschitz,

$$|f(x+h)-f(x)| = O(h^{1-p}), \quad (0 < h: 0 < p < 1),$$
  
 $n^{1-p}a_n = O(1).$ 

then

Moreover, if in the Lipschitz condition O be replaced by o.

$$n^{1-p}a_n \to \text{Lt }\cos \frac{1}{2}p\pi (-x^{1+p}f'(x))/\Gamma(p+1).$$

Let us put

$$f(x) = f_1(x) + f_2(x),$$

where  $f_1(x) = f(x) - f(e)$  in the interval  $(-e \le x \le e)$ , and is zero elsewhere.

Then  $f_2(x)$  satisfies our condition of Lipschitz throughout the whole interval  $(-\pi, \pi)$ . Therefore by Lebesgue's result (loc. cit., § 1 supra) the theorem holds when for f we substitute  $f_2$  in the enunciation. Hence it is only necessary to prove that the theorem is true when for f we substitute  $f_1$ .

Now in the interval  $(e, \pi)$  we have  $f_1(x) = 0$ , and if 0 < t < e, in (t, e) the function  $f'_1(x) = f''(x)$  is bounded, therefore we have

$$f_1(t) = -\int_t^t f'(t) dt = -\int_t^t t^{-1-p} y(t) dt,$$

where y(t) is the bounded function hypothecated in the enunciation. Therefore we may write

$$\int_0^\pi f_1(x) n \cos nx \, dx$$

$$= \operatorname{Lt} \int_t^e f_1(x) \, d(\sin nx)$$

$$= \operatorname{Lt} \left( -f_1(t) \sin nt - \int_t^e f_1'(x) \sin nx \, dx \right)$$

$$= -\int_0^e g(x) x^{-1-p} \sin nx \, dx = -n^p \int_0^{ne} g(t/n) t^{-1-p} \sin t \, dt,$$

since  $|f_1(t)| \le A \int_t^t t^{-1-p} dt$ , where A is the upper bound of |g(x)| in (0, e),

so that  $f_1(t)$ , and therefore also  $f_1(t) \sin nt$ , for fixed n, vanish as  $t \to 0$ .

Now dividing the interval of integration (0, nc) at the point  $2k\pi$ ,

$$\left| \int_{-\infty}^{n\omega} (t/n) t^{-1-p} \sin t \, dt \, \right| = \frac{B}{p} [(2k\pi)^{-p} + (ne)^{-p})],$$

where B is the upper bound of |g(x)| in  $(0, \epsilon)$ . Letting n increase indefinitely this term is therefore numerically  $\leq B(2 h\pi)^{-p}/p$ , which is as small as we please, if k is chosen conveniently large.

Also since g(t/n) + g(+0) boundedly,

$$\int_0^{2k\pi} g(t/n) t^{-1-p} \sin t \, dt \to g(+0) \int_0^{2k\pi} t^{-1-p} \sin t \, dt.$$

Thus finally, letting first n and then k increase indefinitely,

$$\operatorname{Lt} \int_{0}^{\pi} f_{1}(x) n^{1-p} \cos nx \, dx = -g(+0) \int_{0}^{\pi} t^{-1-p} \sin t \, dt \\
= -g(+0) (\cos \frac{1}{2} p\pi) / \Gamma(p+1).$$

which proves the theorem in both its parts.

§ 11. Similarly we have the following theorem :-

THEOREM 10.—If f(x) is an odd function, which in a certain neighbourhood (-e, s) surrounding the origin is such that  $x^{1+p}(df/dx)$  is a bounded function with a unique limit as  $x \to 0$ , and in the remaining part of the interval  $(-\pi, \pi)$  itself satisfies the condition of Lipschitz,

$$f(x+h)-f(x) = O\phi(h^{1-p}), \qquad (0 < h; 0 < p < 1),$$
$$n^{1-p}b_{-} = O(1).$$

then

Moreover, if in the Lipschitz condition O be replaced by o, then  $n^{1-p}b_n \to \text{Lt} \sin \frac{1}{2}p\pi (-x^{1+p}f'(x)/\Gamma(p+1).$ 

It is, in fact, only necessary to follow the reasoning of the preceding article.  $(1-\cos nx)$  taking the place of  $\sin nx$ .

§ 12. We now proceed to give other generalisations of the properties of simple sine and cosine series referred to at the end of § 7. That we have convergence to zero is due to the fact that whatever power of  $x^{-p}$  we take, there is no index which will make this just summable. On the other hand, if a smaller index is used than 1/p, the example of the simple sine and cosine series shows that we must get o and not O.

THEOREM 11.—If f(x) is an even function, which in (-e, e) is such that  $\left| x \frac{df}{dx} \right|^{1/p}$  is integrable (summable) and in the remaining part of the interval  $(-\pi, \pi)$  itself satisfies the condition of Lipschitz,

$$f(x+h)-f(x) = O(h^{1-p}),$$
  $(0 < h; 0 < p < 1),$   
 $n^{1-p}a_n = O(1).$ 

then

Moreover, if in the Lipschitz condition, O le replaced by o, then

$$n^{1-p}a_n \to 0$$
.

In fact, writing g(x) for x df/dx,

$$ef(e)-tf(t)=\int_{t}g\left( x\right) dx+\int_{t}^{\epsilon}f\left( x\right) dx;$$

and, therefore, as in the preceding article, tf(t) = 0 as t = 0.

Thus we get, as in the proof of Theorem 3, or rather in Theorems 5, 7, 9, in accordance with the remarks of § 9, that the convergence of  $na_n$  is virtually the same as that of  $-\int_0^s g(x)(\sin nx/x) dx$ .

We now use the theorem of § 8, p. 439 of my paper "On the Mode of Oscillation of a Fourier Series and of its Allied Series,"\* which tells us that this latter integral when divided by  $n^p$  converges to zero. Hence  $na_n$  divided by  $n^p$  converges to zero, that is

$$n^{1-p}a_n \to 0.$$

THEOREM 12.—If f(x) is an odd function which satisfies the same conditions as in Theorem 11,

$$n^{1-p}b_n\to 0.$$

The argument is precisely the same as that used in proving Theorem 11, except that  $\int_0^s g(x)[(1-\cos nx)/x]dx$  takes the place of  $\int_0^s g(x)(\sin nx/x)dx$ .

Reasoning precisely analogous to that employed in the article quoted at the end of the preceding proof leads to the same order of magnitude of this integral as of the other integral, as is, indeed, pointed out in the article quoted, this integral being related to the allied series as the other is to the Fourier series.

§ 13. In the next two theorems we use, instead of the condition of Lipschitz, the condition of Lipschitz-Dini, namely,

$$\operatorname{Lt}_{h\to 0}\left(\left(\log\frac{1}{h}\right)[f(x+h)-f(x)]\right)=0,$$

the convergence being uniform for all values of x, or as we shall for brevity write it

$$|f(x+h)-f(x)| = o\left(\frac{1}{\log 1/h}\right).$$

THEOREM 13.—If f(x) is an even function, which in (-e,e) is such that x(df/dx) is bounded, and in the remaining part of the interval  $(-\pi, \pi)$  itself satisfies the condition of Lipschitz-Dini,

$$f(x+h)-f(x)=o\left(\frac{1}{\log 1/h}\right),$$

then

$$na_n = O \log n$$
.

Further, if in addition x(df/dx) has a unique finite limit as  $x \rightarrow 0$ , then

$$na_n = o \log n$$

that is

$$na_n/\log n \to 0$$
.

\* 'Lond, Math. Soc. Proc.,' Ser. 2, vol. 12.

The proof of this theorem is precisely similar to that of Theorem 9, using the corresponding result of Lebe-gue's,\* and § 3, p. 436 of my paper "On the Mode of Oscillation of a Fourier Series and of its Allied Series."

**THEOREM 14.**—If f(x) is an odd function, satisfying the same conditions as in Theorem 13,

$$nb_n = O \log n$$

and if, in addition, x(df/dx) has a unique finite limit as  $x \to 0$ , then

$$\operatorname{Lt}_{n\to\infty}(nb_n/\log n)=0.$$

Here, again,  $(1-\cos nx)$  replaces  $\sin nx$  in the part of the integral considered due to the interval (0, e).

[Added December, 1916.—In a communication made to the Société Helvétique, in August, entitled "Sur les intégrales multiples et les séries de Fourier," I remarked that I had occupied myself with the extension to multiple Fourier series of results obtained by myself and others with respect to Fourier series of a single variable, and that I had as yet not found any which did not hold mutatis mutandis in the general case. This is also true of the results of the present paper.]

\* Loc. cit., § 1 supra.

The Corrosion and Electrical Properties of Steels.

By Sir Robert Hadfield, F.R.S., and Edgar Newbery, D.Sc.

(Received September 28, 1916.)

As long ago as 1899, Caspari\* showed that the condition that zinc should dissolve in an acid solution with evolution of hydrogen may be expressed in the form—

Single potential of metal + overvoltage < single potential of hydrogen electrode. (a)

The single potential of zinc in a normal zinc sulphate solution is -0.493 volt, and that of a hydrogen electrode in normal sulphuric acid is +0.277 volt. If a mixture of zinc sulphate and sulphuric acid be taken, the potential of the zinc will become more positive as the concentration of zinc sulphate increases, and the potential of the hydrogen electrode more negative as the concentration of the acid decreases. Since the overvoltage of pure zinc is about 0.7 volt, conditions may be easily adjusted in this way so that solution is exactly arrested and the statement (a) above then becomes an equation.

If a definite solution is used for a series of experiments, then the potential of the hydrogen electrode is constant, and the tendency of the metal to dissolve will be measured by the fixed potential of this hydrogen electrode minus the sum of the overvoltage and the potential of the metal.

Denoting this "solution voltage" by the letter S, we may say generally that the condition that any metal shall dissolve with evolution of hydrogen in the given solution is

S > 0.

and, further, that the rate of solution of the metal is approximately proportional to the value of S.

In order to apply this method of reasoning to the problem of steel corrosion, two assumptions have to be made:—

- (1) That the corrosion factor of a given steel is proportional to its rate of solution in a given acid.
- (2) That the rate of corrosion without evolution of gas is controlled by similar laws to that with evolution of gas.

If these assumptions are even approximately true, then it should be

<sup>\* &#</sup>x27;Zeit. Physik. Chem.,' vol. 30, p. 89 (1899).

possible to obtain a good estimate of the corrosion factor of a given steel by a simple measurement of its overvoltage and single potential in a given acid.

The work described in this communication was undertaken with the idea of examining how far, if at all, these assumptions were justifiable.

## Varietics of Steel Used.

The samples of steel taken were 15 in number, all forged bars, 1 inch diameter and 5 inches long. Discs of ½-inch thickness were sawn off each bar, and a small segment of about 1 cm. chord sawn off each disc. The samples were numbered as follows:—

Steel	No.	Type of steel.
S.C.I.	•••	 Pure iron.
2229	• • •	 Carbon steel, low.
2228		 Carbon steel, medium.
1618/2		 Carbon steel, medium.
898 M/13		 Silicon iron alloy.
3433/2		 High chromium alloy.
1775		 Nickel chromium steel, low carbon.
1795 C		 Nickel chromium steel, medium carbon.
1663 S .		 Nickel chromium steel, high carbon.
3137 D	• • •	 Nickel chromium steel, high carbon.
3125		 Nickel steel, 5 per cent. Ni.
3408		 Nickel steel, 36 per cent. Ni.
1908 D	·	 Tungsten steel.
3435		 Tungsten cobalt steel.
1109 D	• • •	 "Resista," an alloy of 5 per cent. Mn and 15 per cent. Ni.

Full analyses, showing the compositions of these various steels, are given in the Table on p. 58.

### Overvoltage Measurements.

The small segments of steel were smoothed on an emery wheel and a uniformity of surface secured by rubbing on No. 1 emery cloth. This uniformity of surface is necessary for comparative purposes, as the overvoltage is affected to a small extent by the nature of the surface.\*

A short copper wire was soldered to each and covered with white, hard sealing wax, leaving only 1 sq. cm. of the steel uncovered. The overvoltage was then measured by the Back E.M.F. method, as described in 'Trans. Chem. Soc.,' vol. 105, p. 2420 (1914), the electrolyte being N/1 H<sub>2</sub>SO<sub>4</sub>.

Four series of measurements were made with current densities from 2 to 2000 milliampères per square centimetre, and the averages of these four sets

<sup>\*</sup> Pring and Curzon, 'Faraday Soc, Trans.,' 1911.

Sir R. Hadfield and Dr. E Newbery.

Tana of steel	Stool No	Treatment.		   			Analysis.				
		Ü	ప	æ.	øż	<b>P</b> i	Mn.	ć	R	À	ું ક
Pure iron	8.C.I.	As forged		40	-013	-014	\$				
Carbon steel	2220	:	-	.31		1	<b>8</b>				_
Carbon steel	2228	;		90.	1	1	<b>₹</b>		-		
Carbon steel	1618/2	f	•	91.		1	3				
Silicon material	898 M/13		Π.	39.00	643	035					
Chromium steel (high Chromium)	3133/2	775° Farnare	•	1	1	1	1	12.84			
Nickel steel	3125	As forged		1	1	!	÷.	1	2 00		
Nickel steel	1796 H	830° Furnace		1	1	1	1 .35	1	89.61		
Nickel steel	3408	As forged		90	12	8	28	1	36.38		
Nickel chromium steel	1775			1		ı	.13	1.81	3.41		
Nickel chromium steel	1796 C	795 Furnace		.10	970	041	.42	1.79	3.43	_	
Nickel chromium steel	1663 B	795° Furnace	•	.12	1	1	.12	3	0-8		
	3137 D	795° Purnace		71.	1	1	.12	2 .50	27.5		
" Resista" (Fe-Ni-Mn alloy)	1109 D	As forged			1	1	200	1	15.00		
Tungsten chromium steel	1908 D	796° Furnace		1	1		02	4-00	1	17.0	~
Tungsten chromium cobalt steel	3435	775° Furnace	-	1	1	1	1	8 62	1	16.1	8 7

Summary of Analyses of Specimens.

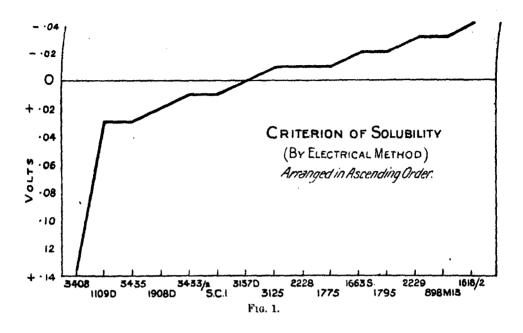
of readings are given in the following Table, the current density being given in milliampères per square centimetre and the overvoltage in volts.

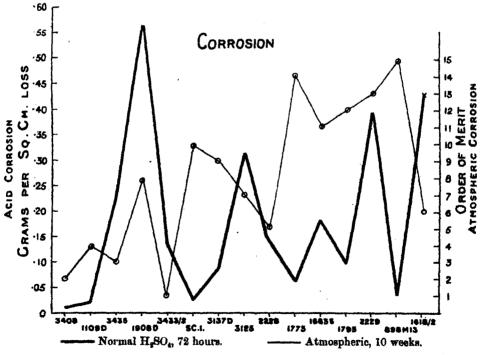
Current density.	S.C.I.	2229	2228	1618/2.	898 M/13.	3483/2.	1775.	1795 C
2	0 -24	0 .23	0 .30	0 .21	0 .22	0 26	0.20	0.18
4	0.25	0.23	0.21	0.21	0 .22	0 .26	0.20	0.19
в	0.26	0.23	0.22	0.21	0.22	0.26	0.21	0.19
10	0.26	0 .24	0.22	0.22	0.22	0.26	0.21	0.19
20	0.27	0 .24	0.22	0.22	0.22	0.26	0 21	0.19
50	0.27	0 .24	0 .28	0.22	0.22	0 .27	0.23	0.30
100	0 .27	0.24	0 .23	0 22	0 .22	0 .27	0.22	0.19
200	0.27	0 .24	0.22	0.22	0.22	0.27	0.22	0.19
400	0 .28	0.24	0.22	0.21	0 .22	0.27	0.23	0.18
1000	0 .27	0 24	0.21	0.20	0 .21	0.28	0.21	0.17
2000	0 .26	0.23	0.21	0.19	0.20	0.27	0.20	0.16

Current density.	1668 S.	3137 D.	3125.	8408.	1908 D.	8485.	1109 D
2	0 ·19	0.19	0.18	0.50	0 .21	0 .21	0 · 19
4	0.19	0.20	0 .19	0 .22	0.22	0 22	0.20
6	0.20	0.21	0.19	0.23	0.22	0 .28	0.20
10	0.20	0.21	0.20	0.23	0.28	0 .24	0.21
20	0.20	0 .22	0 .20	0.53	0.28	0 .24	0 21
50	0.21	0.22	0.21	0.28	0.28	0.25	0.21
100	0.21	0.28	0 21	0.22	0.24	0 .25	0 21
200	0.21	0.23	0 .31	0.21	0.24	0 .25	0.21
400	0.21	0.23	0.21	0.20	0 24	0 .25	0.20
1000	0.21	0 23	0.19	0.18	0.23	U ·25	0.19
2000	0.20	0 .22	0.18	0.17	0.22	0.28	0.18

## Single Potential Measurements.

After measuring the overvoltage, the electrodes were washed with distilled water, dried, and repolished with emery cloth as before. The potential of each was then measured in a N/1 H<sub>2</sub>SO<sub>4</sub> electrolyte against a mercurous sulphate electrode containing the same solution. Measurements were made by means of the same apparatus as used for overvoltage, the anode A being disconnected, and readings taken every minute for 5 to 10 minutes until constant for 3 consecutive minutes. Measurements were also taken in an electrolyte consisting of N/1 FeSO<sub>4</sub> + N/1 H<sub>2</sub>SO<sub>4</sub>, but no appreciable difference was observed. After deducting the difference of potential between a normal mercurous sulphate electrode and a normal hydrogen electrode, the following values were obtained for the single potentials of the steels against a standard hydrogen electrode:—





F1G. 2.

Steel.	Potential.	Steel.	Potential.	Steel.	Potential.
S.C.I. 2229 2228 1618/2 898 M/13	volt. -0 '28 -0 '26 -0 '21 -0 '25 -0 '25	8433/2 1775 1795 C 1663 S 8187 D	volt. -0 ·25 -0 ·21 -0 ·20 -0 ·21 -0 ·19	3125 3408 1908 D 3435 1109 D	volt. -0·19 -0·06 -0·19 -0·18 -0·16

In order to combine these measurements with the overvoltage measurements, the question arises as to what current density should be taken as standard. Since the local currents set up during most forms of steel corrosion are probably very feeble, it is perhaps advisable to take the values for the overvoltage at the lowest current densities used. On adding these overvoltages to the corresponding single potentials, we obtain the values of —S\* for each electrode. These are arranged in order of magnitude in the following Table:—

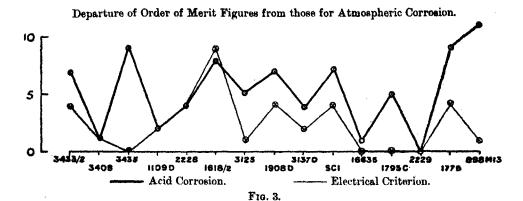
No.	Steel.	-S.	No.	Steel.	-8.
1	3408	volt. +0:14	9	2228	volt. -0 01
2	1109 D	+0.03	10	1775	-0.01
3	8485	+0.03	îĭ	1663 8	-0.02
4	1908 D	+0.02	12	1795 C	-0.02
5	8483/2	+0.01	18	2229	-0.08
6	8.C.1.	+0.01	14	898 M/13	-0.08
7	3137 D	0.00	15	1618/2	0·04
8	3125	-0.01			

#### Corrosion in Acid.

For these measurements, the larger segments of the discs cut off from the bars were used. One face of each disc was smoothed down on a carborundum wheel, rubbed with emery as before, weighed carefully, and the remainder of the disc covered with a coating of wax. All the discs were then laid, polished side up, on the bottom of a large glass dish, and 3 litres of N/1 H<sub>2</sub>SO<sub>4</sub> poured in, the temperature being 15±1° C. throughout the whole experiment.

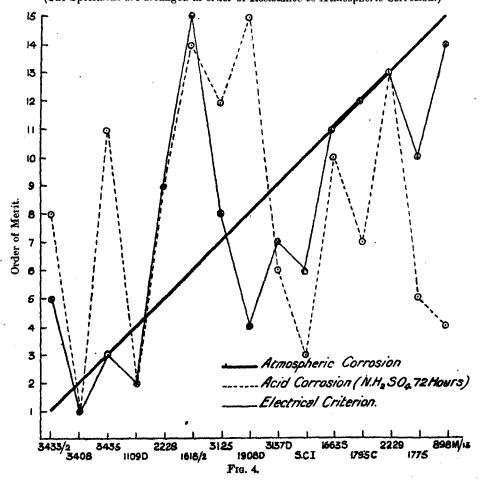
After 72 hours the discs were removed, washed, the wax cleaned off, and the discs dried and weighed. The loss in weight per square centimetre of exposed surface is given in the following Table:—

<sup>\*</sup> While S measures the corrodibility, -S measures the resistance to corrosion. The Table is arranged in this way in order to correspond with the other Tables.



Order of Merit—Resistance to Corrosion.

(The Specimens are arranged in order of Resistance to Atmospheric Corrosion.)



Steel.	Loss in grm.	Steel.	Loss in grm.	Steel.	Loss in grm.
8.C.I. 2229 2228 1618/2 898 M/13	0 ·024 0 ·400 0 ·142 0 ·432 0 ·084	8438/2 1775 1795 C 1663 S 8137 D	0 ·132 0 ·062 0 ·096 0 ·182 0 ·088	3125 8408 1908 3485	0 ·314 0 ·008 0 ·564 0 ·280

## Atmospheric Corrosion.

The steel bars from which the discs had been sawn off were placed in a horizontal row in a box with the worked ends protruding and left exposed to the laboratory atmosphere for 10 weeks during the months of May, June, and July. At the end of that time none of the bars showed any appreciable rust except on the worked ends, and since patches on these ends had been polished by the rubbing action of the upper part of the saw, the variation in corrodibility of the polished and rough metal could be observed. They were carefully examined with the aid of a Coddington lens and arranged in order of corrodibility, as follows:—

No.	1	3433/2	Quite bright. No rust.
,,	2	3408	Faint, but uniform light brown coloration.
,,	3	3435	Bright, slight traces of rust.
,,	4	1109 D	Bright, rusting a little more marked.
,,	5	2228	Bright, patches of rust visible.
**	6	1618/2	Polished parts bright, large rust patches.
"	7	3125	Polished parts bright, larger rust patches.
,,	8	1908 D	Polished parts bright, rest covered with rust.
99	9	3137 I)	Polished parts black, rest covered with rust.
٠,	10	S.C.I.	Polished parts black and partly rusted, rest quite rusted.
17	11	1663 S	Polished parts black and much rusted.
,,	12	1795 C	Quite covered with rust, thin over polished parts.
,,	13	2229	Quite covered with rust, polished parts not visible.
13	14	1775	Badly rusted, thick uniform coating.
>7	15	898 M/13	Badly rusted, thick uniform coating.

The Table on p. 64 shows the order of resistance to corrosion of the steels as determined by these three methods.

If the object of experiments on corrosion be considered to be the determination of the alloys which best resist the action of the atmosphere, then the figures in the third column of the Table must be taken as standard, and those in the other columns judged as good or bad according to their nearness or otherwise to those in the third.

Reviewing the Table as a whole, in four cases the electrical and acid methods give identical results, in 10 cases the electrical method gives better results than the acid method, and in one case only (No. 1618/2), the acid

Steel No.	Electrical method.	Corresion in soid.	Atmospheric corresion.
S.C.I.	6	3	10
2229	18	18	18
2228	9	9	5
1618/2	15	14	6
898 M/13	14	4	15
8488/2	5	8	i
1775	10	5	14
1795 C	12	7	12
1668 S	11	10	11
3187 D	7	6	9
3125	8	12	7
3408	1	1	2
1908 D	4	15	8
3485	3	11	3
1109 D	2	2	4

method gives a slightly better estimate than the electrical though both are wide of the mark. This is evidently due to the presence of 1 per cent. Mn in the specimen, since this metal is only attacked slowly by the atmosphere owing to the formation of a protective oxide coating, while it dissolves with ease in acid and also has a high negative solution potential.

In four cases only does the electrical method agree with atmospheric corrosion, but the acid method only agrees in one case and the deviations are generally much greater with this method.

#### Notes on Individual Alloys.

S.C.I., Pure Iron.—The resistance of this to the action of acid seems to be connected with its high overvoltage, and its non-resistance to atmospheric corrosion may be due to the presence of some substance in the air which reduces the overvoltage. After treatment with acid the surface was quite smooth but dull.

2229, Low Carbon Steel.—In this case only, all three methods agree in showing the alloy to be very liable to corrosion. Large patches were eaten out by the acid.

2228, Medium Carbon Steel.—Both electrical and acid methods underestimate the corrosion-resisting powers of this alloy. The surface was pitted by the acid in patches.

1618/2, Medium Carbon Steel, 1 per cent. Mn.—This has already been referred to. The surface was very deeply pitted and eaten into by the scid.

898 M/13, Silicon Iron Alloy.—The acid test in this case gives a very false impression as to the corrodibility. The surface remained smooth and bright. The electrical method gives a much better idea.

3433/2, High Chromium Alloy.—Here again, both methods greatly underestimate the corrosion-resisting powers of this alloy, the acid method giving the more incorrect estimate, the surface being decidedly pitted after treatment. This was the only alloy which was quite unchanged by the atmospheric test.

1775, Cr Ni Steel, Low Carbon.—The corrodibility is underestimated by the electrical method and very badly by the acid method. After treatment with acid the surface was almost smooth. With this exception, all the nickel steels have been well placed by the electrical method, while half of them are badly placed by the acid method.

1795 C was slightly pitted, 1663 S deeply pitted, and 3137 D left almost smooth by the acid test.

3125, Nickel Steel, 5 per cent. Ni, was very badly attacked by the acid, specially round the edges. Though the overvoltage is low, the negative single potential is also low, and hence the electrical method places this alloy much higher on the scale than the acid method, and nearer the value indicated by atmospheric corrosion.

3408, Nickel Steel, 36 per cent. Ni.—The low negative single potential of this alloy, due to the high percentage of nickel, places it easily first by the electrical method, and its appearance was quite unchanged by the acid test. In the atmosphere the coloration produced is probably due to a thin protective coating of nickel oxide.

1908 D, Tungsten Steel.—The ready solubility of this, and also of No. 3435, which also contains tungsten, is surprising. Both have fairly high overvoltages and low negative single potentials, and hence the electrical method gives a much better estimate of the corrosion-resisting powers.

1109 D, Manganese Nickel Steel.—The figure for the acid test with this alloy is doubtful, as owing to the extreme toughness a disc could not be out off, and the experiment was made with a small chipping.

#### Advantages and Disadvantages of the Electrical Method.

#### (a) Advantages:-

- 1. This method certainly gives a better estimate of the ability of an alloy to resist atmospheric corrosion than the acid immersion method.
- 2. When once the apparatus is fitted up a sample can be examined in 10-30 minutes, while at least two hours is necessary for the acid test.
- 3. By the addition of certain elements with the object of raising the overvoltage and of others with the object of lowering the negative single potential, there appears to be a better chance of attaining the ideal of a rustless steel than by merely trusting to a single measurement for determining corrodibility.
  - 4. Very small samples, less than 1 grm., may be used.

# (b) Disadvantages:-

- 1. The apparatus needed is much more complicated and expensive than that required for the acid test, and greater skill in manipulation is necessary.
- 2. The differences in the values of S obtained are not great enough for suitable grading of the alloys.
- 3. Slight errors in measurement may cause large differences of position in the corrodibility scale.
- 4. Where a large number of samples have to be tested at the same time, the acid immersion method can probably be worked more quickly, specially as the electrodes for the electrical method require careful preparation.

The overvoltage apparatus (loc. cit.) can be considerably simplified. The voltmeter V may be dispensed with, and the potentiometer P<sub>2</sub> replaced by a sliding resistance coil. A calomel or mercurous sulphate electrode may be used instead of the more troublesome hydrogen electrode, a unipivot galvanometer may replace the reflecting galvanometer and shunt G, and the commutator X can be fixed directly on the spindle of a small electromotor and driven easily at a high speed.

It may be better to use still lower current densities, say from 0.1 to 10 milliampères per square centimetre and extrapolate to find the overvoltage at zero current density. Possibly also the measurement of the overvoltage and the single potential in a solution of a weaker acid such as acetic may give results more comparable with atmospheric corrosion and also give greater variation in the values of S obtained. The liability to atmospheric corrosion is reduced by polishing the surface of a metal, owing to the fact that the overvoltage is raised, and it is generally true that any process or addition which raises the overvoltage of a metal also reduces its tendency to corrode. The galvanising of iron is a case in point, zinc having a very high overvoltage.

There are, of course, so many different causes of corrosion that one cannot hope for a method which will give reliable information on corrodibility in all cases. Again, referring to the comparison Table, we see that the electrical method only places one alloy more than four out, while the acid method makes nine such mistakes out of the 15 cases. At the same time, in five cases the electrical method makes a mistake of four places, and this cannot be regarded as satisfactory. It is hoped that the method may be further developed so as to give more reliable information.

Other points which might be considered are :-

- (1) The average overvoltage.
- (2) The maximum overvoltage.
- (3) The current density required to produce maximum overvoltage, but

conclusions deduced from such considerations would not have the same theoretical foundation as those obtained by the method already described.

It is evident that the assumptions made at the beginning of this paper are only fulfilled to a small extent. The first is certainly somewhat wide of the facts if the given acid is N/1 H<sub>2</sub>SO<sub>4</sub>. It may be nearer the mark when some other acids are used, and it is possible that, with suitable choice of solvents, reliable information may be obtained with regard to corrodibility under different circumstances. The present paper deals only with atmospheric corrosion, and the conclusions arrived at are not intended to apply to other cases (sea water, strong acids, etc.). The second of the two assumptions appears more justifiable than the first, as it is largely on this second that the electrical method is based. The solution or corrosion of a metal is intimately associated with the exchange of electrical charges, and the tendency to corrosion is measured by the potential differences between these charges. When the acid test is employed, the overvoltage of the sample is considerably lowered as soon as the surface becomes attacked, and local currents are set up due to slight non-homogeneity of the alloy, thus greatly increasing the rate of solution. In the electrical method, the surface of the metal or alloy is quite unchanged during the overvoltage measurements if the current density is kept low, and is not appreciably affected by the five minutes' acid immersion when the single potential is measured. Hence the resistance of the alloy to the beginning of corrosion is determined, and it must, of course, be remembered that this is not usually the same after corrosion has once started.

There is no reason why the electrical method should not be employed with non-ferrous alloys and metals, but further experiment with different electrolytes is needed before any standardisation will be possible.

A recent paper by one of the writers of the present paper is given in the 'Journal of the Iron and Steel Institute,' No. 1, 1916, entitled "The Influence of Carbon and Manganese upon the Corrosion of Iron and Steel." Much useful information with regard to the effect of tap water and sea water is there presented.

# Monoclinic Double Selenates of the Nickel Group.\* By A. E. H. TUTTON, D.Sc., M.A., F.R.S.

(Received November 23, 1916.)

# (Abstract.)

In this paper the results are given of the investigation of the double salts potassium nickel selenate, rubidium nickel selenate, easium nickel selenate, and ammonium nickel selenate, each containing six molecules of water of crystallisation, forming the group of the series R<sub>2</sub>M(SeO<sub>4</sub>)<sub>2</sub>,6H<sub>2</sub>O in which M is nickel. The results are absolutely in line with all those already published for the complete monoclinic double sulphate analogous series with 6H<sub>2</sub>O, and for the isomorphous magnesium and zinc double selenate groups. The morphological and physical properties exhibit the progression in accordance with the atomic weight of the alkali metal which has been so clearly brought out by the previous work, and the ammonium salt is shown conclusively to belong to the isomorphous series, and to exhibit the peculiar traits described in connection with the other ammonium salts of this monoclinic series already dealt with.

Symmetry.—This is the same for all the four salts, as for all the other groups of double sulphates and selenates dealt with, namely, Class 5, prismatic-holohedral, of the monoclinic system.

Crustal Elements - These are -	Crustal	Elements -	_These	are	
--------------------------------	---------	------------	--------	-----	--

	Axial angle \$.	Axial ratios. a : b : c.
KNi selenate RbNi selenate NH4Ni selenate CsNi selenate	104° 27′ 105 20 106 17 106 11	0 '7467 : 1 : 0 '5059 0 '7395 : 1 : 0 '5031 0 '7395 : 1 : 0 '5048 0 '7288 : 1 : 0 '4998

The axial angle of the rubidium salt is almost exactly midway between the axial angles for the potassium and easium salts, corresponding to direct progression with the atomic weight of the interchangeable alkali metals. The axial ratios for the rubidium salt are also intermediate.

The axial ratios for the ammonium salt are very close to the analogous values for the rubidium salt, and the axial angle of the ammonium salt is nearly identical with that of the essium salt.

<sup>\*</sup> For full paper see 'Phil. Trans.,' A (not yet published).

Habit.—Potassium nickel selenate and cæsium nickel selenate exhibit characteristic habits, very distinct from each other, dependent on the relative development of the faces of two forms, the basal pinakoid  $c\{001\}$  and  $q\{011\}$ . In the case of the potassium salt  $c\{001\}$  predominates, either conferring a tabular habit or, if the prism faces  $p\{110\}$  are fairly high, giving a flat top and base to the vertical prism (which is parallel to axis c); while the  $q\{011\}$  faces form merely small side-corner truncations. In the cæsium salt, on the other hand, the faces of the basal pinakoid  $c\{001\}$  form only more or less narrow elongated strips, with large  $q\{011\}$  faces on each side of them, the two forms, together with low and narrow faces of the clino-pinakoid  $b\{010\}$ , forming a prism parallel to the inclined axis a. The rubidium salt exhibits an intermediate type, in which the faces of  $c\{001\}$  and  $q\{011\}$  are more or less equally developed. The ammonium salt also usually resembles the rubidium salt, but its intermediate character has a wider range than the very distinctive intermediate type presented by rubidium nickel selenate.

Interfacial Angles.—The interfacial angles of rubidium nickel selenate are intermediate in value between those of the analogous potassium and consists a progressive change of angle following the replacement of potassium by the heavier and still heavier atoms of rubidium and consists. Thirty-six quite different angles have been measured and compared, and the average values of the changes which they show for each replacement, and the maximum amount of change of angle, are given below:—

Replacement.	Average change.	Maximum change.
K by Rb K by Co K by NH4	47	57' 119 110

Remembering that the atomic weights of the three metals are K = 38.9, Rb = 84.9, Cs = 131.9, and that the increments of atomic weight are Rb - K = 46, and Cs - K = 93 (double 46), it is obvious that the average and maximum increments of angles are directly proportional to the increments of atomic weight of the metals interchanged.

The ammonium salt proves its isomorphism, although not eutropism, by the fact that the average and maximum changes, when NH<sub>4</sub> replaces K, are not quite so large as when easium replaces potassium, that is, the change is of precisely the same order as for the metallic replacements, and not outside their limits.

Volume.—The volume and dimensions of the unit cells of the structural apace-lattice, relatively expressed by the molecular volume and the topic

axial ratios	, are,	perhaps,	the	most	important	of	all	the	morphological
constants.	They	are given	belov	v :					

,	Molecular volume.	Topic axial ratios, $\chi : \psi : -$ .
KNi selenate	206 •14	6 1677 : 8 2598 : 4 1786
RbNi selenate	216 96	6 '2588 : 8 '4561 : 4 '2542
NH <sub>4</sub> N iselenate	216 .53	6 - 2520 : 8 - 4543 : 4 - 2678
CsNi selenate	229 17	6 8817 : 8 6878 : 4 8878

The volume and dimensions of the unit cell are thus found to show a regular and somewhat accelerating progression from the potassium salt, through the rubidium salt, to the essium salt, and the values for the ammonium salt are very close indeed to those for the rubidium salt. The importance of this latter fact will be pointed out in the concluding paragraph of this abstract.

The Optical Ellipsoid.—The ellipsoid, which graphically represents the optical properties, enlarges as potassium is replaced, first by rubidium and then by cæsium. At the same time it rotates progressively about the symmetry axis b. Starting with the potassium salt, the ellipsoid is situated with one of its other two principal axes (those which lie mutually at right angles in the symmetry plane) not far from parallel to the vertical crystal axis c; when the potassium is replaced by rubidium the ellipsoid rotates so that the axis in question moves away 3° further from the vertical direction, and when the rubidium is in turn replaced by cæsium, the ellipsoid rotates in the same direction nearly 7° further, the progression being thus an increasing one. For the ammonium salt the position is nearly truly vertical.

Optic Axial Angles.—The optic axial angles have been measured for seven wave-lengths of light, and found to show a similar slightly increasing progression with the atomic weight of the alkali metal. The optic axial angle for the ammonium salt is slightly larger than that for the rubidium salt.

Refractive Indices and Double Refraction.—The refractive indices have also been determined for seven wave-lengths. They also progress from the potassium to the easium salt, the acceleration being, in this case, so considerable that a curious effect is produced by the simultaneous more direct progress (almost in simple proportion) of the double refraction which occurs. The double refraction—the difference between the  $\gamma$  and  $\alpha$  indices for the same wave-length, sodium light being taken for the comparison—is 0.0246 for KNi selenate, 0.0192 for RbNi selenate, 0.0175 for the NH<sub>4</sub>Ni salt, and 0.0094 for the CsNi salt. The effect referred to is that, while the  $\alpha$  and  $\beta$  indices of

the rubidium salt are higher than those of the potassium salt, in consequence of the first progression, the difference between the extreme indices is so curtailed by the second progression (diminution of the double refraction) that the  $\gamma$  indices are just slightly less than those of the potassium salt, and the mean refractive index works out to be exactly the same for both potassium and rubidium salts.

Molecular Optical Constants.—The true progression in refractive power is, however, best shown by the molecular refraction. This, indeed, is probably the most important of all the optical constants, just as the volume and directional dimensions of the unit cell are the most important morphological constants. The values in Gladstone units are given below:—

	Molec	Mean value.		
1	α	β	γ.	$\frac{1}{3}(\alpha+\beta+\gamma)$
KNi selenate	106 · 10	107 -96	111 ·10	108 :39
RbNi selenate	112 08	114 '07	116 .20	114 12
NH <sub>4</sub> Ni selenate	113 .70	115 .56	117 45	115 .57
CsNi selenate	122 90	124 14	125 .03	124 .02

The true progression with the atomic weight of the alkali metal is clearly shown by these constants, and the fact that the molecular refraction of ammonium nickel selenate is almost identical with that of rubidium nickel selenate is as impressive as, and is doubtless connected with, the closeness to identity of the volumes and directional dimensions of the unit cells of the similar space-lattices of the two salts.

#### Concluding Remarks,

In conclusion, two points from the above results may be specially emphasised. Firstly, the remarkably quantitative manner in which the law of progression is indicated in the cases of the alkali metallic salts. For it has been shown that the average and maximum amounts of all the changes in interfacial angles when potassium is replaced by cæsium are exactly double those for the replacement of potassium by rubidium, corresponding precisely to the change of atomic weight, which is almost exactly double (93 to 46). That the ammonium salt is really isomorphous with the alkali metallic salts is proved by the fact that when ammonium is substituted for potassium the average and maximum changes of angle are no more, and, indeed, just slightly less, than if cæsium were introduced instead of potassium.

The second point worthy of emphasis is the extreme closeness of the molecular volumes and the topic axial ratios of the rubidium and ammonium

salts of the group, representing the volumes and edge dimensions of the unit cells of the monoclinic space-lattices of the two crystal structures. The values thus indicate very perfect congruency and almost identity of the two structures. It will be shown in a separate communication, immediately following this paper, that this result, in conjunction with the precisely similar facts observed concerning the ammonium and rubidium salts of every group investigated by the author, including the rhombic group of simple alkali sulphates, has an important bearing on the theory of valency volumes; for that theory is entirely incapable of explaining it.

X-Ray Analysis and Topic Axes of the Alkali Sulphates, and their Bearing on the Theory of Valency Volumes.

By A. E. H. TUTTON, D.Sc., M.A., F.R.S.

(Received November 20, 1916.)

One of the most interesting facts brought to light in the course of the author's crystallographical investigations of the rhombic sulphates and selenates of potassium, rubidium, cæsium, and aumonium, and of the monoclinic double salts containing those simple salts in combination with the sulphates and selenates of dyad-acting metals (Mg, Zn, Fe, Ni, Co, Mn, Cu, and Cd), is the approximation in structure which has invariably been observed between the rubidium salt of any group and the ammonium salt of that same group. This striking fact is again emphasised by the results for the nickel group of double selenates,\* laid before the Royal Society on the same day as this present communication, and of which an Abstract immediately precedes this paper. While considerable differences occur between the structural dimensions of the potassium, rubidium, and cæsium salts of the group—differences which have been shown to follow the order of the atomic weightst

<sup>\*</sup> See 'Phil. Trans.,' A (not yet published).

<sup>†</sup> Instead of "atomic weights" we may substitute with equal validity "atomic numbers" (the numbers of the elements according to their sequence in the Periodic Table). For the atomic numbers of K, Rb, and Cs are 19, 37, and 55, and their differences are similarly related, Rb-K=18, Cs-Rb=18, and Cs-K=36 or twice 18. Indeed, it is probable that there is an intimate connection between this crystallographic law of the author and the law of Moseley, that the properties of an element are defined by the atomic number, which is equal to the number of units of positive electrical charge in the atomic nucleus.

of the alkali metals (K = 38.85, Rb = 84.9, Cs = 131.9, and Rb - K = 46, Cs-Rb=47, Cs-K=93, or twice 46), so that the rubidium salt is always intermediate—the ammonium salt has without exception proved to possess structural dimensions almost identical with those of the rubidium salt, the central member of the group. By structural dimensions are meant the directional dimensions and the total volume of the unit cell of the spacelattice, the same type of which is common to the whole rhombic or monoclinic isomorphous series. The total volume is represented by the molecular volume (the quotient of the molecular weight by the density of the crystal), and the three directional dimensions of the cell in space are known as the topic axial ratios, or topic axes. The experimental basis of the molecular volume (molecular weight being known) is a very accurate determination of the density of the most perfect attainable crystal. The topic axial ratios require for their calculation (in addition to the molecular volume) the crystal elements (crystal-axial angles and ratios), which are derived from very accurate measurements of the external interfacial angles of perfectly developed crystals.

For a series of isomorphous salts, such as the rhombic normal sulphates of the alkali-metallic family group of the periodic classification, R<sub>2</sub>SO<sub>4</sub>, where R may be potassium, rubidium or cæsium, there can be no possible doubt that the type of structure, that is of space-lattice, is identical. Its symmetry is the same for all the members of the group, but the dimensions of the elementary cell vary progressively with the atomic weight or atomic number of the interchangeable alkali metals; and correspondingly the interfacial angles also differ slightly and progressively, in accordance with very definite rules which have been established by the author.

When, however, we introduce the radicle ammonium, NH<sub>4</sub>, instead of an alkali metal, and produce the isomorphous ammonium salt, the possibility has been suggested that the case may not be strictly comparable with the substitution of rubidium or cæsium for potassium. It is just conceivable that the observed similarity of symmetry and crystal angles may be accompanied by a considerable opening up of the structure, such as, for instance, by the introduction of the extra atoms of nitrogen or hydrogen in the form of new layers. That is, it might be a case of a very different sort of structure being produced as regards dimensions and arrangement, but outwardly conforming to the same type of rhombic symmetry, with a fortuitous close similarity in external crystal angles. Although, however, this is a possibility, it is highly improbable. It is true that the quality of the isomorphism of ammonium sulphate is so far different from that between potassium, rubidium, and cæsium sulphates as not to be subject to the law

of progression with the atomic weight or atomic number of the metal, for we are now dealing with a non-metallic radicle group NH<sub>4</sub>. The case is defined by saying that the ammonium salt, while truly isomorphous, does not belong to the exclusive "eutropic" group of the metallic salts, the term eutropism having been applied to the isomorphism of strictly analogous members of the group (their interchangeable elements belonging to the same family group of the periodic classification), which follow the law of progression with the atomic weight or atomic number of the interchangeable constituents both as regards morphological and physical (optical and other) constants.

But the author has shown that although the ammonium salt is not eutropic with the salts of the alkali metals, its molecular volume and topic axial ratios are indeed strictly comparable with those of the alkali metallic salts. That the ammonium salt is truly isomorphous with the alkali-metallic salts is strikingly shown by the fact that not only is the type of symmetry identical and the axial ratios very close (see Table on p. 79), but the average change of angle (mean for 37 measured angles) on replacing potassium by ammonium is not even quite so great as when potassium is replaced by cresium, and the maximum change of interfacial angle follows the same rule. The angular change on substituting ammonium for potassium is, however, naturally greater than when rubidium is introduced instead of potassium, for this latter (Rb) replacement gives rise to only half as much change of angle as when cæsium is introduced for potassium, in accordance with the law of progression for the alkali metals, which law is very beautifully and directly expressed by To make the point clear, the actual figures for the sulphates are given in the following short Table. It should be remembered that the difference of atomic weight or of atomic number between K and Cs is just double that between K and Rb.

Average and Maximum Angular Changes.

				Average.	change.	Maximu	m change
For replace	ment of K	in <b>K<sub>2</sub>80</b> ,	by Rb	0°	9′	0°	26′
,,	,,	17	NH	0	14	0	38
	29	**	Ca	a	18	1 0	50

Precisely similar facts are shown in the monoclinic double sulphate and selenate series, in which the angular changes are much larger; the precision with which the average and maximum changes for the cassium replacement are double those for the rubidium replacement is truly remarkable, in every

group investigated, while the ammonium replacement approaches in effect the cæsium interchange. (See Table in preceding Abstract, p. 69).

If there had been some disturbance of the structure, such as would be provoked by the insertion of additional layers, one would have expected much more disturbance of the interfacial angles than this, even had the type of symmetry been left unaffected (which would have been improbable). Hence, there was every reason to surmise that the internal structural dimensions also had suffered no crucial change, and that they were faithfully indicated by the topic axial ratios. Now, when we make the comparison of these ratios and of the molecular volumes of the four salts we obtain the result stated at the opening of this communication, namely, that the values for the ammonium salt are almost identical with those of the rubidium salt. This will be clear from an inspection of the Table on p. 79. From this, and · from similar relationships which have been observed by the author for the ammonium and rubidium salts of every group of double sulphates and selenates, it has been concluded that the structures of the ammonium and rubidium salts are not only similar but practically congruent. If they could be imagined as shadows (non-material) and one such ghostly space-lattice could be moved over and through the other consequently without interference, it could be brought into actual identity with that other.

Before proceeding to indicate the great significance of this, it should be stated that there is further independent information available to show that it is a real fact. It has been shown by the author that the ammonium and rubidium salts, of the two great rhombic and monoclinic isomorphous series studied in detail, exhibit a remarkable facility for the formation of mixed crystals.\* The analogous potassium and rubidium salts, or the rubidium and cæsium salts, show very little such tendency to crystallise together, and the potassium and cæsium salts, which differ most in molecular volume and topic axial ratios, practically never crystallise together. G. Wulff† has also independently discovered the fact as regards potassium and rubidium sulphates, obtaining perfect mixed crystals of these salts, while he found potassium and cæsium sulphates to be totally immiscible, which he attributes to the great difference in their molecular volumes; he, too, obtained only very imperfect mixed crystals of either ammonium or rubidium sulphate

<sup>\*</sup> Indeed the rhombic form of ammonium selenate (which salt usually crystallises exceptionally in a monoclinic form, being dimorphous) isomorphous with potassium, rubidium, and casium selenates, has only hitherto been obtained by the author in large crystals when admixed with more or less rubidium selenate. It is for this reason (inability to prepare the pure rhombic form) that ammonium selenate is not included in this comparison.

<sup>† &#</sup>x27;Zeitschr. für Kryst. Min.,' vol. 42, p. 558 (1906).

with potassium or cæsium sulphate. Further, T. V. Barker has shown, in a beautiful series of researches, that the facility for forming overgrowth crystals or parallel growths of one salt of an isomorphous series on another is dependent on congruency of structure, as indicated by closeness of molecular volume and topic axial ratios; and that the rubidium and ammonium salts of the same acid (sulphates, chromates, and perchlorates were studied) exhibit the property par excellence, while the corresponding potassium and cæsium salts either form no such over- or parallel growths at all, or do so to a very low minimum extent.

Hence, we are compelled to conclude, the evidence being overwhelming, that the crystal structures of ammonium and rubidium sulphates (and of the analogous double sulphates or selenates containing these two alkali bases and the same dyad-acting metal) are almost identical, isostructural, that is, congruent to a remarkable degree. But this conclusion obviously means that the two atoms of rubidium are replaced by the 10 atoms of 2NH4 without any opening up of the structure. In other words, the structure must either be already sufficiently open to permit of the insertion of the eight additional atoms, or the volume of the two ammonium radicle groups must be approximately the same as that occupied by the two rubidium atoms.

This conclusion has an important bearing on the valency volume theory of Barlow and Pope,† as has frequently been pointed out in the author's memoirs. No adequate explanation has been given of the difficulty. The essence of the theory is that each valency in a given compound has the same volume, and that, therefore, the atomic volumes of combined elements are directly proportional to their valencies. The theory is, of course, entirely inconsistent with Kopp's idea of molecular volume. Thus, in K<sub>2</sub>SO<sub>4</sub> the two monadic potassium atoms are each supposed to occupy unit volume, the four dyadic oxygen atoms each to occupy two volumes, and the sulphur atom is considered, somewhat arbitrarily, to be also only dyadic and to occupy

two volumes; the total volume would thus be 2+8+2=12. Similarly, the two rubidium and existing atoms in the isomorphous salts would occupy the same relative volumes of two out of twelve; and the relative total volumes, as expressed directionally by the "equivalence parameters" employed by Barlow and Pope (who discard topic axial ratios), are also practically identical for the three salts. The theory does not account at all for the considerable increase

<sup>\* &#</sup>x27;Journ. Chem. Soc.,' vol. 89, p. 1120 (1906), and 'Mineralog. Mag.,' vol. 14, p. 235 (1907), and vol. 15, p. 42 (1908).

<sup>+ &#</sup>x27;Journ. Chem. Soc.,' vol. 89, p. 1675 (1906); vol. 91, p. 1150 (1907); vol. 93, p. 1528 (1908).

in molecular volume on passing from the potassium salt through the rubidium to the cæsium salt, corresponding to the very considerable rise (more than tripling) in the atomic weight of the metal, and to the tripling of the atomic number, and indeed ignores it.

In their very first paper Barlow and Pope take\* the case of the sulphates and selenates of potassium, rubidium, and cæsium as an example of the working of their theory; they omit all reference to ammonium sulphate, however. They employ the author's experimental data, and give a Table, which is reproduced below, of the "equivalence parameters" x, y, z, which they calculate like topic axial ratios, except that they use the sum of the valencies, the valency volume W, instead of the author's molecular volume V, together with the author's crystal-axial ratios. It will appear from this Table that any one and the same parameter for the three different salts of each group (sulphate or selenate) remains almost unaltered. The average

Barlow and Pope's Equivalence Parameters for R<sub>2Se</sub>O<sub>4</sub>.

	v.	W.	x : y : x.
K-804	64 .91	12	2 ·2109 : 2 ·1977 : 2 ·8468
Rb-SO.	73 .34	12	2 2049 : 2 1899 : 2 8648
O828O4	84 .58	12	2 ·2003 : 2 ·1826 : 2 ·8777
K <sub>2</sub> SeO₄	71 -87	12	2 -2207 : 2 -2083 : 2 -6204
Rb-SeO4	79 -94	12	2 -2147 : 2 -1957 : 2 -8412
Cs-SeO.	91 .09	12	2 '2112 : 2 '1900 : 2 '8524

difference shown by any one of the three parameters for the two extreme (potassium and cæsium) salts of each group is less than 1 per cent. Indeed, the maximum difference over the whole six salts, including that due to the replacement of sulphur by selenium, is only just 2 per cent. for the third parameter, and it is only 1 per cent. for the first parameter, and 1.3 per cent. for the second parameter. The real directional changes, however, as shown by the topic axial ratios (Table on p. 80), are 10 per cent. in either group, and 12 per cent. over the two groups (from K<sub>2</sub>SO<sub>4</sub> to Cs<sub>2</sub>SeO<sub>4</sub>), while the real change in total volume is as much as one-third. In connection with this Table, Barlow and Pope say specifically that the interchangeable elements of the same group of the periodic system are represented by spheres of atomic influence of nearly the same size as compared with the sphere volumes of other constituents.

In the latest memoir, contributed by Mr. Barlow+ to the 'Mineralogical

<sup>\* &#</sup>x27;Journ. Chem. Soc.,' vol. 89, p. 1724 (1906).

<sup>† &#</sup>x27;Mineralog. Mag.,' vol. 17, p. 314 (1916).

Magazine,' a disposition is shown, in referring to the first X-ray results of Prof. Bragg, to admit that those results demonstrate the value of the constant, molecular volume. For he states: "When isomorphous substances of similar atomic composition are compared, close similarity of the pattern formed by the atomic centres of a given kind common to the compared bodies is associated with a marked difference of scale, viz. of actual dimensions. Thus the distances separating the sulphur atoms in potassium sulphate will not be the same as those separating the atoms in exist unsulphate; corresponding dimensions of the two bodies will be approximately in the ratio of the cube roots of the respective molecular volumes." Yet on the next page, very illogically, Mr. Barlow again recommends the use of the Barlow and Pope equivalence parameters to represent the changes, in which parameters not the molecular volume but the valency volume (identical for the whole series) forms the volume factor, the result shown being consequently an infinitesimal change.

Now, it will be at once apparent that if we replace Rb<sub>2</sub> by 2NH<sub>4</sub> we shall, according to the valency volume theory, be replacing two unit volumes by 10 atoms of volume 14, taking nitrogen at its lower triadic valency, and, therefore, as of volume 3, and hydrogen as 1, the whole salt then having a volume of 24; if nitrogen be pentadic, as is more logical and more in accordance with chemical facts, clearly four more units of volume must be added, making 28. That is, according to the valency volume theory, and on the lower estimate, we double the volume, from 12 to 24, on passing from rubidium sulphate to ammonium sulphate. This, however, has been shown by the author not to occur, but that, on the contrary, the volumes of the ammonium and rubidium salts are almost identical and closely congruent.

It has appeared to the author that in the X-ray spectrometric analysis of crystals, brought to such perfection by Prof. W. H. and Mr. W. L. Bragg,\* we have a new method of attack, which affords a crucial test of the validity, on the one hand, of the author's conclusions based on his experimental results and the conceptions of molecular volume and topic axial ratios, and, on the other hand, of the valency volume theory of Barlow and Pope. The author therefore suggested to Prof. Bragg that an X-ray analysis of the rhombic alkali sulphates and selenates would prove of extreme value; Prof. Bragg happily concurred and arranged for such an analysis to be carried out in his laboratory, with crystals supplied by the author, many of them being the actual crystals employed in the author's published investigations. The work has been carried out by Prof. A. Ogg and Mr. F. Lloyd Hopwood, and a first paper of results has been published in the 'Philo-

<sup>\* &#</sup>x27;X-rays and Crystal Structure,' G. Bell and Sons, 1915, 2nd edition, 1916.

sophical Magazine' for November, 1916, vol. 32, p. 518. These results, it may be said at once, have proved conclusively that the ammonium and rubidium salts are, indeed, practically iso-structural, the actual dimensions (absolute volumes and distances in space) of the space-lattice elementary cells having been measured, and found to be precisely as closely identical as is indicated relatively by the molecular volumes and the topic axial ratios. The dimensions for the potassium and cæsium salts, moreover, are found to be considerably different, just as much so, in fact, as is suggested by the molecular volumes and topic axial ratios for those salts. The actual directional dimensions in space, as measured directly by the X-ray spectrometer, are wonderfully close to the author's values for the topic axial ratios. These latter constants, therefore, are both justified and verified. On the other hand, there can be no other conclusion than that the valency volume theory is not based on fact, and is fallacious.

The actual numbers, both of the topic axial ratios and of the X-ray spectrometric dimensions for the sulphates, are given in the accompanying Tables, an inspection of which cannot fail to be impressive and conclusive in the sense just indicated. The important values to be compared are those in the right-hand portion of the second (middle) Table (topic axes when  $\psi$  for  $K_2SO_4 = 1$ ), with the lengths of the sides of the unit rhomb in the third (bottom) Table. The actual volumes in the last column of the bottom Table show very clearly the closeness of the volumes of the rubidium and ammonium salts, just as do the molecular volumes given in the first Table.

The actual lengths of the elementary cell edges given by Prof. Ogg and Mr. Hopwood, expressed in terms of  $10^{-8}$  cm., happen to be on the scale of 10 times greater than that of the relative distances given by the topic axial ratios; indeed, if " $10^{-7}$ " be written after each of the author's topic axial ratios (when  $\psi$  for  $K_2SO_4 = 1$ ), these latter relative values become converted

Densities, Molecular	Volumes and	Crystal Axial	Ratios	(Tutton).
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Salt.	Density.	Molecular weight (H = 1).	Molecular volume.	Ratio of axes, $a : b : c$ .
K <sub>2</sub> SO <sub>4</sub>	2 .866	173 -04	64 -91	0 · 5727 : 1 : 0 · 7418
Rb <sub>2</sub> SO <sub>4</sub>	8 .612	265 -14	78 ·84	0 '5728 : 1 : 0 '7485
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	1 .772	181 .20	74.04	0 .5635 : 1 : 0 .7319
Ca <sub>3</sub> 8O <sub>4</sub>	4 246	859 14	<b>84</b> · 58	0 . 5712 : 1 : 0 . 7581
K <sub>9</sub> SeO₄	8 .067	219 -82	71 .67	0 . 5781 : 1 : 0 . 7819
Rb-8eO4	8 .902	811 -92	79 94	0 .5708 : 1 : 0 .7386
Ca <sub>3</sub> SeO <sub>4</sub>	4 ·456	405 .92	91 .09	0 '5700 : 1 : 0 '7424
į.		1 1	i .	

Topic Axial Ratios (Tutton).

Salt.	Direct results of formulæ. $\chi : \psi : \omega$ .	$\psi \text{ for } \mathbf{K}_2 \mathbf{SO}_4 = 1.$ $\chi :  \psi :  \omega.$
K <sub>2</sub> 8O <sub>4</sub>	8 ·0617 : 5 ·8460 : 8 ·9657	0 -5727 : 1 -0000 : 0 -7418
Rb <sub>2</sub> SO <sub>4</sub>	3 .1778 : 5 .5528 : 4 .1562	0 .5944 . 1 .0887 : 0 .7774
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> Cs <sub>2</sub> SO <sub>4</sub>	8 · 1788 : 5 · 6413 : 4 · 1289	0 5946 : 1 0552 : 0 7728
Cs <sub>2</sub> SO <sub>4</sub>	3 *8215 : 5 *8149 : 4 *3792	0 6218 : 1 0877 : 0 8191
K,SeO4	8 ·1802 : 5 ·5491 : 4 ·0613	0 -5949 : 1 -0380 : 0 -7597
Rb <sub>2</sub> SeO <sub>4</sub>	3 2792 : 5 7450 : 4 2488	0 6134 : 1 0746 : 0 7987
Ca-SeO.		0 .6390 : 1 .1210 : 0 .8828

### Absolute Dimensions of Space-Lattice Cell (Ogg and Hopwood).

Salt.	Length of sides of unit rhomb.			Volume of unit
	a	b	c.	rhomb.
	The second secon	** v 1000 <del>000 de april 1000</del>	and the second s	Management of the second agreement of the second and the second and
	em.	em.	em.	c.c.
K.SO.	5 ·731 × 10 ·-8	10 '008 × 10~8	$7.424 \times 10^{-8}$	425 ·78 × 10-24
Rb <sub>0</sub> SO <sub>4</sub>	5 ·949 × 10-8	$10.394 \times 10^{-8}$	$7.780 \times 10^{-8}$	481 ·14 × 10-24
(NH <sub>4</sub> ),SO <sub>4</sub>	5 ·951 × 10 <sup>-8</sup>	10 '560 × 10-#	$7.729 \times 10^{-8}$	485 ·71 × 10-94
Cs.SO.	6 ·218 × 10-8	10 '884 × 10-8	$8.198 \times 10^{-8}$	554 '88 × 10 <sup>24</sup>

into the actual distances in space. Remembering this, the differences between the two sets of constants are wonderfully small, less than one in a thousand (the actual differences varying from 0.07 to 0.08 per cent.). Too much stress must not be laid on this, however, as the actual numbers in the last resort depend on the angular values for the reflections observed in the X-ray spectrometer, a long list of which is given by Prof. Ogg and The agreement between these angles and those calculated Mr. Hopwood. from the figures in the third Table is amply adequate, however, to sub-The calculation of the length a of K2SO4 stantiate the facts stated. directly from the X-ray measurements, given later on p. 83 as an example, afforded, for instance, the value 5.73, with a possible error not exceeding 1 Hence, the results are fully trustworthy. The values given in the middle Table for the topic axial ratios, in which the unit is taken as the  $\psi$  value for the first salt of the series, potassium sulphate, are new ones now given for the first time, derived by use of the author's latest determinations of the density of the crystals by the Retgers immersion method. The values formerly given,\* however, which depended on the less trustworthy pyknometer density determinations, nowhere show appreciably greater differences from the X-ray values, the greatest being 0.09 per cent., as against 0.08 per cent. in the case of the new values.

<sup>\* &#</sup>x27;Journ. Chem. Soc.,' vol. 83, p. 1067 (1903).

The formulæ used in determining the topic axes of these rhombic crystals, referred to in the middle Table, were as under:—

$$\chi = \sqrt[3]{\frac{a^2V}{c}}, \quad \psi = \sqrt[3]{\frac{\overline{V}}{ac}}, \quad \omega = \sqrt[3]{\frac{\overline{c^2V}}{a}},$$

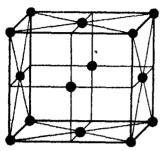
where a, b, c are the crystal-axial ratios and V is the molecular volume. They relate to the unit cell of rectangular rhombic form, that is, a rectangular brick-like block with three different edge-lengths, corresponding to the three crystal axes a, b, c. As topic axial ratios are relative lengths, the author reduces them to their simplest form by dividing out by the  $\psi$  value of the potassium salt, the first member of the series, the topic axial ratios in the case of this salt becoming then identical with the crystal-axial ratios. Indeed, it has to be remembered that the topic axial ratios are in the same proportion to each other as the crystal-axial ratios, being modified correspondingly to the molecular volume, so as to show how the latter is directionally distributed.

In the first paper on these sulphates, in the year 1894, the author\* pointed out that there was a considerable amount of evidence that the full crystal unit, the smallest edifice possessing the complete details of symmetry of the crystal structure and which (considered as a point) by its regular repetition affords the space-lattice, was composed of four molecules of R<sub>2</sub>SO<sub>4</sub>. Now, it is exceedingly interesting that Prof. Ogg and Mr. Hopwood find this to be a fact, indubitably indicated by their X-ray analysis. The rectangular parallelepipedal cell, the edges of which are the a, b, c of their measurements, is that formed by taking analogously situated atoms, whether these be metallic, sulphur, or oxygen atoms, one from each set of four molecules to act as their representative point. the author's later papers the idea of the necessity for identifying molecules at all in the crystal structure was not referred to, as the purely geometrical theory of crystal structure, now complete, regards the structure as essentially But the author has always considered this to be carrying geometry too far, further than either the chemistry or the physics of the organised solid, the crystal, warrants. It is a satisfaction, therefore, to find that the work of Prof. Bragg and his colleagues now shows that there is a real advantage in and necessity for thus marking off the molecules, if only in order to obtain a correct idea of the structure which is essential to the crystal as such.

The work of Prof. Ogg and Mr. Hopwood is not yet complete as regards the details of the structure, but sufficient has been done to render it almost certain

<sup>\* &#</sup>x27;Journ. Chem. Soc.,' vol. 65, p. 662 (1894).

that the sulphur atoms are situated at the corners and centres of the faces of the unit cell, as shown in the accompanying figure. Owing to the angles



Arrangement of the sulphur atoms in unit cell of spacelattice of alkali sulphates.

at the centre of the face of the rhomb bounded by a and b edges being near  $60^{\circ}$ , it is to be remarked that the sulphur atoms would thus exhibit a pseudo-hexagonal structure in planes parallel to the basal plane, the face (001). It is also stated in their paper as probable that the metallic atoms are also arranged in hexagons. This is particularly interesting, for Fedorov has proposed a pseudo-hexagonal structure for these rhombic sulphates, as being indicated by his crystallo-chemical analytical of finding the method correct setting of crystals.

In deference to this, the author\* recalculated the topic axial ratios for such a pseudo-hexagonal space-lattice, using the new densities which had just been determined; the points of the lattice were the same as for the rectangular lattice, but the diagonal distances between them were taken as forming four sides of the hexagon (two equal pairs), along with one of the rectangular axial directions only, which furnished the other two sides (one equal pair, but not quite equal to the others), such a lattice having angles of nearly exactly 60°. These facts are doubtless not unconnected with the remarkable manner in which the crystals often display a hexagonal appearance, sometimes by twinning (as in the well-known triplets of potassium sulphate, which resemble short hexagonal prisms doubly capped by pyramids), and sometimes by mere habit on the part of the single crystals (as in the case of the apparently hexagonal double pyramids of rubidium sulphate), the angles in the primary prism zone, formed by the faces of p {110} and b {010}, being very nearly 30°. The pseudo-hexagonal topic axial ratios do not enable a comparison to be made with the measurements of Prof. Ogg and Mr. Hopwood, hence the necessity for now publishing the new values corresponding to the rectangular form.

The mode of arriving at the results of Prof. Ogg and Mr. Hopwood may be briefly described. The actual distances between the centres of the sulphurtatoms forming the corners of the rectangular elementary cell, or, in other

<sup>\* &#</sup>x27;Journ. Chem. Soc.,' vol. 87, p. 1188 (1905).

<sup>†</sup> The metallic or oxygen atoms may here be equally as well specified as the sulphur atoms, provided they are similarly analogously chosen, one from each set of four molecules; for the same space-lattice applies in common, being formed by any representative analogous points, one from every structural unit composed of four molecules.

words, the distances between the consecutive planes in each of the three sets of parallel planes of atoms corresponding to the faces of the three primary pinakoids (100), (010), and (001), were obtained from the measurements of the glancing angles of reflection of the X-rays from these faces (in reality from the interior planes of atoms parallel to the faces). The now well-known Bragg equation is employed:—

$$n\lambda = 2 d \sin \theta$$

where n is the order of spectrum (first, second, or third),  $\lambda$  is the wave-length of the X-radiation used (in this case from a palladium anticathode),  $\theta$  is the glancing angle of reflection of the X-rays, and d is the distance in question between successive planes of atoms. We have only to insert the observed value of the angle  $\theta$ , the wave-length  $\lambda$  (already determined by the use of the crystals best worked out by Prof. Bragg, such as the alkali chlorides, and confirmed by independent methods) of the particular line of the spectrum of the radiation used, and the numerical order of the spectrum, in order at once to obtain the distance d required. For instance, when the value of  $\lambda$  for the line employed in the spectrum from the palladium anticathode used was  $0.584 \times 10^{-8}$ , and the glancing angle for this radiation in the second order spectrum reflected from the (100) face of potassium sulphate was  $5^{\circ}$  51', the value of d for planes of atoms parallel to this face was found to be:—

$$d_{(100)} = 5.73 \times 10^{-8}$$
 cm.

That this corresponds to a structural unit composed of four molecules is proved by the following:—

Molecular weight of  $K_2SO_4 = 173.04$ ; density 2.666.

Ratio of crystal-axes a:b:c=0.5727:1:0.7418.

Mass of the hydrogen atom =  $1.64 \times 10^{-24}$  grm.

Mass of unit rhomb of 4 molecules K<sub>2</sub>SO<sub>4</sub>

 $= 4 \times 173.04 \times 1.64 \times 10^{-24} = 1135.1 \times 10^{-24} \text{ grm.},$ 

also

 $abc \times 2.666 = 1135.1 \times 10^{-24} \text{ grm.}$ 

Then from the known axial ratio values of a:b:e we find

 $a = 5.731 \times 10^{-8}$  cm.,  $b = 10.008 \times 10^{-8}$  cm.,  $c = 7.424 \times 10^{-8}$  cm.

Volume of unit rhomb =  $abc = 425.78 \times 10^{-24}$  c.c.

The equality of the value of  $\alpha$  and that for  $d_{(100)}$  obtained above shows that the assumption that there are four molecules of  $K_2SO_4$  in the elementary cell is correct.

The work in Prof. Bragg's laboratory on the corresponding selenates has been interrupted for the present, but, as the author's values for the morphological constants on the same rectangular basis as regards the unit cell will be required when it is resumed, they are given in the two Tables on pp. 79 and 80.

As regards the valency volume theory, there is now much evidence, from the work of other investigators, that the theory can no longer be entertained. It has always appeared to the author to be unlikely to represent the truth. Until, however, definite experimental evidence of a decisive character was forthcoming, such as that now afforded by the X-ray analysis, the author has not felt justified in expressing his views. It appeared most unlikely that a theory could be correct which does not admit the undoubted very considerable increase in volume (one-third of its bulk) which occurs on replacing potassium in potassium sulphate by cæsium, the equivalence parameters of Barlow and Pope showing an almost negligible change, as already pointed out in connection with the Table of these parameters given on p. 77. A considerable increase was in any case to be expected, corresponding to the increase in complexity and in material content of the atom (probably by the addition of further rings or other distributions of negative electrons, in accordance with Moseley's law), indicated by the rise in atomic weight from 38.85 to 131.9, and of the atomic number from 19 to 55. Yet, while taking practically no note of this, the theory asserts that the volume of the oxygen atom, of the low atomic weight 16 and atomic number 8, is twice as great as that of the exiting atom, or whatever alkali atom is present in combination with the oxygen.

Moreover, it has been possible to put forward the theory only by the aid of what cannot be called anything else than quite unwarrantable arithmetical manipulation of the crystal-axial ratios, the arbitrary dividing or multiplying of certain ratios by various numbers to suit the exigencies of the theory. This manipulation has been defended by the authors of the theory and is maintained and used extensively by Barlow in the very latest memoir on the subject," as justifiable on the ground that a certain amount of arbitrariness exists in the choice of the crystal axial planes. It is argued that planes corresponding to the manipulated ratios may be considered equally as valid for axial planes as those chosen by the crystallographer who measured the crystals. This contention, however plausible, is not to be substantiated. There is always some good reason for the choice of particular planes for axial planes, such as the fact that these planes were generally the vastly predominating ones developed as faces, and were \* 'Mineralog. Mag.,' vol. 17, p. 314 (1916).

parallel or otherwise definitely related to the cleavage planes discovered Moreover, Fedorov\* has recently indicated means by which the proper setting of a crystal, which involves the proper choice of axial planes, can be checked and in doubtful cases determined, so that there is no longer any excuse for the incorrect choice of these fundamental planes. In general, the decision afforded by Fedorov's method is given in favour of simplicity and low indices for the other planes developed on the crystal. Barker, who has made a special study of Fedorov's method, and has worked in his laboratory at Petrograd, has shown, however, in typical cases taken from among those put forward by Barlow and Pope, that the new crystal elements arrived at by their manipulations lead in general to greater complexity of the indices of the other faces, in some cases, indeed, grotesquely so. This indicates the inherent improbability that the manipulation was justifiable. Barker has further shown that ninety of the hundred examples put forward by the supporters of the theory are tainted with this arbitrary and unwarrantable manipulation of the axial ratios. Further, that on the most generous basis not more than five cases out of the hundred can in any sense be regarded as being in consonance with it, and not one of them actually demands the theory as the sole or even the best explanation.

A very important contribution to the subject has also been made by Prof. Theodore Richards (Harvard), in two memoirs dealing with the subject which he has made his own, the compressibility of atoms. He shows that the valency volume theory is directly opposed to the results of his investigations, and that it leads to extraordinary and highly improbable conclusions. Richards, indeed, can find no plausible reason why each valency in a given compound should have the same volume. He gives one remarkable illustration of the impossible situation in which the theory lands its supporters, that of the relationship between benzene and tetrabromobenzene. There is no reason why all the remaining carbon and hydrogen atoms in benzene should nearly double their volume when four atoms of bromine are substituted for hydrogen, as the valency volume theory demands. The more reasonable explanation, as all Kopp's work shows, is that the atomic volume of bromine in combination is much larger than that of hydrogen, as we should obviously expect it to be from its much greater atomic complexity; but they are the same, each of unit volume, according to the valency volume theory.

Richards shows, moreover, that the most striking argument advanced by

<sup>\*</sup> E. S. Fedorov, 'Crystallochemical Analysis' (Russian), 1914; 'Zeitschr. für Kryst. Min.,' vol. 53, p. 337, and vol. 54, p. 17 (1914).

<sup>† &#</sup>x27;Journ. Chem. Soc.,' vol. 107, p. 744 (1915).

<sup>† &#</sup>x27;Journ. Amer. Chem. Soc.,' vol. 35, p. 381 (1913), and vol. 36, p. 1686 (1914).

Barlow and Pope, derived from the results of Le Bas for the molecular volumes of the liquids of normal paraffins just above their melting points, is an entire fallacy. He shows that (quite apart from the fact that these are liquids and not solids, and that an arbitrary temperature is chosen for the comparison) the agreement between the molecular volumes and the volumes calculated on the Barlow-Pope basis of vol. C = 4 vol. H, is no better than would occur on almost any other assumption. For instance, if the volume of the carbon be taken as twice that of the hydrogen, the agreement is practically as good, and if carbon be taken as five times hydrogen, the agreement is twice as good.

The memoirs of Richards are particularly interesting, and relevant to the questions raised in this communication, as they deal specifically with the isomorphism of the ammonium and potassium salts. He considers its explanation quite beyond the reach of the valency volume theory, which gives to ammonium nine volumes (according to Richards, but seven according to Barlow and Pope, who take nitrogen arbitrarily as triadic instead of pentadic), but to potassium only one volume. He finds it hard to see how any sort of analogous symmetry could be constructed in the two cases under the circumstances. The work on compressibility of atoms, however, suggests that the five atoms making up the radicle NH<sub>4</sub> possess together about the same volume as the potassium (or, better still, according to the author's work, rubidium) atom, and are compressed by their mutual affinities into a shape not unlike that occupied by the compressed and distorted alkali metallic atom.

Richards finally shows that the volume occupied by a solid is dependent on the variable forces which come into play, and which are not arbitrarily determined but are inherent in the atoms, and that every change in affinity must produce its corresponding change in volume. On the other hand, Barlow and Pope assume that the spheres of influence of atoms expand and contract to fit their theory of valency volumes, for which there is no plausible reason. Their theory takes no account of numerous facts such as: that less cohesive elements have large molecular volumes and large compressibilities; that among isomers the more volatile are also the more compressible, are less dense, and possess less surface tension and greater coefficients of expansion; that, in general, the exhibition of greater chemical affinity involves greater diminution in volume; and the very large internal pressures which must exist in solids. Indeed, Richards concludes that the doctrine of valency volume is irreconcilable with a broader view of the nature of solids and liquids and the mechanism of chemical change.

Barlow and Pope replied\* to the first paper of Richards, but after the \* 'Journ. Amer. Chem. Soc.,' vol. 36, p. 1675 (1914).

second they published only a short note,\* in which the statement was made that a weighty reason rendered further discussion at that time (August, 1914) futile, namely, that "during the last year or two a method for the practical determination of crystal structure has been developed by Laue, and W. H. and W. L. Bragg, which gives every promise of ultimately leading to very precise information concerning the arrangement of the atoms in a crystalline structure. . . . Further discussion may well be postponed until the important developments which are promised have had time to mature." This time would appear now to have arrived, and the results of Prof. Ogg and Mr. Hopwood, obtained in the laboratory of Prof. Bragg, have furnished the crucial test, which is decisively against the valency volume theory.

Careful study of the memoirs of Barlow and Pope, and of the expedients employed therein, leads to the anticipation of the possibility of the suggestion being put forward, to explain the now incontrovertibly proved isostructure of ammonium and rubidium sulphates, that although there are 24 valency volumes in (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and only 12 in Rb<sub>2</sub>SO<sub>4</sub>, the actual spheres of atomic influence in the former are on a smaller scale than in the latter, namely, on a one-half scale, thus affording in the total the same volume. Such an assumption, however, would be even more arbitrary than that denounced by Richards in the case of tetrabromobenzene; or than that which they made concerning the replacement of K in K1 by NH<sub>4</sub> (according to which the volume of the iodine suffers a shrinkage of five-sevenths of the bulk which it occupies in the potassium salt), and which has been shown by Barker† to be most unreasonable. Indeed, the assumption would not be merely arbitrary, but positively absurd.

In the opening words of his last memoir, communicated to the Royal Society only very shortly before his lamented demise, Sir William Ramsay; stated: "It is now almost universally acknowledged that the valency of an element is due to its being associated with one or more electrons." This idea as to the nature of valency, which assigns a practical meaning, that of an attaching electron or electrons, the oscillating valence-electron, to the older idea of a "bond," is one which is rapidly developing from the great progress now being made in our knowledge of the nature of the atom, due very largely to the researches of Sir J. J. Thomson, Sir E. Rutherford, van den Broek, Bohr, and Moseley. Indeed, it is a natural corollary to the beautiful structure of the atom, as we now know it from these researches; and especially from the revelation in the work of Moseley (unhappily his last)

<sup>\* &#</sup>x27;Journ. Amer. Chem. Soc.,' vol. 36, p. 1694 (1914).

<sup>† &#</sup>x27;Journ. Chem. Soc.,' vol. 101, p. 2496 (1912).

t 'Roy. Soc. Proc.,' vol. 92, p. 451 (1916).

of the important function of the atomic number in corresponding to the positive nuclear charge, and thereby determining the number of negative satellite electrons in the electrically stable atom. The idea of the valence-electron or electrons was most interestingly worked out by W. C. Arsem\* in 1914, and its logical outcome was to show that the valency of an atom is a natural result of the dynamic relations between molecules and the atoms of which they are composed. We shall, doubtless, hear a great deal more about this view of valency in the near future. It is impossible to conceive, however, of any connection whatever between valency of such a nature and the volume of the atom or its sphere of influence. On the other hand, the conception of atomic and molecular volumes, and their directional expression in topic axial ratios, is in complete harmony with this new knowledge of the structure of the atom.

Finally, the decisive result of the X-ray analysis of the sulphates of the alkalis may be accepted as substantiating a truth which had already been indicated by a growing body of evidence, derived from all sides, namely, that the valency volume theory of Barlow and Pope has no foundation in fact. On the other hand, the indications of the constants molecular volume and topic axial ratios, for the members of any isomorphous series of crystalline substances, are proved to express accurately the structural relations of such substances.

# Summary of Conclusions.

- 1. An X-ray spectrometric analysis of the orthorhombic crystals of the alkali sulphates, R<sub>2</sub>SO<sub>4</sub>, where R represents potassium, rubidium, cæsium, and ammonium, carried out in the laboratory of Prof. W. H. Bragg by Prof. A. Ogg and Mr. F. Lloyd Hopwood, has indicated that four molecules of R<sub>2</sub>SO<sub>4</sub> are contained in the unit rectangular cell of the space-lattice, as was suggested by the author in the year 1894.
- 2. The atoms of sulphur occupy the corners of the rectangular cell and the middle point of each side; they lie, therefore, in planes separated at distances equal to half the lengths of the sides. The planes of sulphur atoms parallel to the (001) face (the basal plane) are of pseudo-hexagonal structure, the points (atomic centres) being arranged in nearly regular hexagons, a structure which has been suggested by Fedorov and adopted by the author (Tutton). The metallic atoms (K, Rb, or Cs) are also probably arranged in nearly regular hexagons.
- 3. X-ray spectrometric measurements, based on the accurate knowledge of the wave-length of the X-radiation employed (a specific line in the radiation from a palladium anticathode), of the actual lengths (absolute distances in

<sup>\* &#</sup>x27;Journ. Amer. Chem. Soc.,' vol. 36, p. 1655 (1914).

space) of the edges of the rectangular orthorhombic cells of the space-lattice (distances apart of the centres of the S atoms in the three rectangular axial directions, or of the metallic or oxygen atoms, when similarly analogously chosen, that is, one from each set of four molecules to represent the crystal unit), agree perfectly with the topic axial ratios for these salts determined by the author. A new series of the latter constants is now published for the rectangular space-lattice, based on later, more refined density determinations than those given in 1903; both the old and the new values are in excellent agreement with the X-ray measurements.

- 4. The congruency or close approximation to identity of the structures of rubidium and ammonium sulphates, indicated by the molecular volumes and topic axial ratios published by the author (not only for these simple sulphates, but for every pair of double sulphates and selenates in which the R bases are rubidium and ammonium, as in the example of ammonium nickel and rubidium nickel selenates brought forward in a separate paper\*), is thus confirmed by absolute measurement by the X-ray spectrometric method. The absolute volumes of the unit cells of the space-lattices of the two salts are within 1 per cent. of identity, just as are the molecular volumes, and the absolute lengths of the three edges for the two salts are correspondingly close to each other, and in a manner precisely like that shown by the topic axial ratios.
- 5. It is thus fully substantiated that the constants molecular volume and topic axial ratios afford true indications of the relative volume and dimensions of the elementary space-lattice cells, in the cases of the crystal structures of isomorphous series.
- 6. As the volume of the unit cell of ammonium sulphate should be at least twice that of rubidium sulphate according to the valency volume theory of Barlow and Pope (that is, if we assume triadic valency for nitrogen, since the sums of the fundamental valencies of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and Rb<sub>2</sub>SO<sub>4</sub> are respectively 24 and 12), and more than twice if nitrogen be pentadic (the volumes then being 28 to 12), whereas the volumes of the unit cells of the two salts are now proved by direct X-ray measurement to be nearly identical, it is obvious that the valency volume theory does not represent a law of nature. A crucial test has thus now been applied, and the decision is against the theory.

<sup>\*</sup> See preceding Abstract.

# Address of the President, Sir J. J. Thomson, O.M., at the Anniversary Meeting, November 30, 1916.

It is a pious custom, hallowed by long usage, that your President at the Anniversary Meeting should begin by paying, on behalf of the Society, tribute to the memory of those of our members who have been taken from us since our last Meeting. This year our losses have been almost unprecedentedly severe, and are so numerous that it is impossible, in the time at our disposal this afternoon, to describe at all adequately the work those we have lost have accomplished, and their manifold claims to our respect; for this we must look to the Obituary Notices which have been, or will be, published by the Society. My words must be few and inadequate.

Shortly after the last Meeting, by the death of the Right Hon. Sir Henry Enfield Roscoe, we lost one who, for more than half a century, had been foremost in promoting the interests of Science and Education. He was renowned not only for his researches, but also for his success as a teacher and expositor; he organised at the Owens College, Manchester, a school which was for long the most important centre of research in chemistry in this country.

As a student at the Owens College in the seventies I have a vivid recollection of the influence he exerted on the development of what is now the Victoria University of Manchester, as well as on the extension of the chemical industries of the district. He was a wise and unbiassed counsellor, ever ready to help in any project which he thought would improve the condition of the country.

By the death of Sir William Ramsay we have lost a chemist whose discovery of the rare gases in the atmosphere has been among the greatest contributions made by this country to science. The founder of a great school of research at University College, a great teacher, a man of unbounded energy and remarkable independence of judgment, his loss, while full of vigour and ideas, has deprived English Science of one of its greatest personalities.

Dr. Henry Debus was a veteran of veterans among teachers of chemistry, and had been a Fellow of the Society for more than fifty years.

Prof. Silvanus Thompson had for long played a prominent part in the development of electrical science in the country, he was a man with many gifts, literary and artistic, as well as scientific, a most successful teacher, and a remarkably clear expositor, whether with tongue or pen. He had an unrivalled knowledge of the literature of physics, which enabled him to

render invaluable service to the Society as Chairman of the 'Catalogue of Scientific Papers.'

In Mathematics we have lost Dr. Benjamin Williamson and Prof. Esson, who combined with their mathematical knowledge powers of organisation and administration which made them play a great part in their respective universities.

The University of Edinburgh, as well as our Society, suffered a severe loss by the death of Sir William Turner. In addition to being a great anatomist, he was a man of much influence and a very successful administrator, and was for many years foremost in all questions relating to Scottish universities.

Medical science has lost Sir Victor Horsley and Sir William Lauder Brunton. Horsley was a pioneer in the surgery of the brain, and showed all the surgeons of the world how to operate on the brain and spinal cord. He gave his life to help his country in this war, going to give much-needed help to our troops at the front in Mesopotamia, and there he died at Masara, in July. Lauder Brunton was renowned for his contributions to medical science and for his skill as a physician.

The death of Dr. Keith Lucas through an accident, when flying, adds another name to the Roll of Honour of Fellows of the Royal Society who, during the war, have lost their lives in the service of the country. At the beginning of the war he joined the Royal Aircraft Factory at Farnborough, and devoted his remarkable inventive power to making improvements in the equipment of aeroplanes; in this work he was very successful. He possessed unrivalled powers of design in physical apparatus for the investigation of physiological problems, and this faculty enabled him to make researches in regions of physiology which were beyond the reach of other workers. He delivered the Croonian Lecture in 1912. His death leaves a gap in physiological science, and in the circle of his friends, which it will be difficult indeed to fill.

Physiology has sustained another loss by the death of Prof. BRODIE, of the University of Toronto, who made important investigations on the kidney, of which he gave an account in the Croonian Lecture for 1911.

By the death of the Right Honourable Sir James Stirling, a Senior Wrangler, for many years a judge in the Chancery Division, and from 1900 to 1906 a Lord Justice of Appeal, we have lost a wise counsellor, and one who was ever ready to help the Society with his legal knowledge and experience.

Mr. ROLAND TRIMEN, a Darwin Medallist, and at one time Curator of the South African Museum, was well known both for his own researches in natural history and for his association with those of Darwin and Wallace.

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Dr. Scott, formerly Secretary to the Meteorological Council, had been for long closely associated with the progress of meteorological science in this country.

Sir WILLIAM HENRY POWER, K.C.B., for some time Medical Officer to the Local Government Board, was a leading authority on the question of public health, and received the Buchanan Medal in 1907. There are few, if any, in this country who have done more than Sir William Power to advance the cause of scientific hygiene.

Sir CLEMENTS MARKHAM was one of the veterans of Arctic exploration, and a former President of the Royal Geographical Society.

Prof. Judd was a distinguished geologist who was for long Professor at the Royal College of Science.

Prof. H. H. W. Pearson, whose name appears both in the list of newlyelected Fellows and the Obituary list, was an enthusiastic botanist, whose premature death will be a great blow to the progress of botany in South Africa, where he was a professor.

Mr. Charles Booth rendered great services to the country by his remarkably interesting and important investigations on Social Statistics.

By the death of Prof. METCHNIKOFF, a Foreign Member and Copley Medallist of the Society, Science has lost a great leader and France one of her most eminent citizens. He will ever be remembered by his investigations on inflammation and on immunity to infective germs and the poisons produced by them. To quote the words of Sir Ray Lankester, "he was especially honoured and revered by every Zoologist in the world, for it was to him that we owed the demonstration of the unity of biological science and the brilliant proof of the invaluable importance to humanity of the structure and laws of growth of the lower animals, which he had pursued from pure love of the beauty and wonder of the intricate problems of organic morphology."

The death of Prince Galitzine and Prof. Backlund has deprived our ally Russia of two of the most prominent and distinguished of her men of science.

Prince Galitzine, who died shortly after election as Foreign Member, had, it is hardly too much to say, revolutionised the science of Seismology, while Dr. Backlund, the distinguished head of the great observatory of Pulkowa and renowned for his researches on Encke's comet, had many warm friends in this country and rendered great services to the English astronomers who went to Russia to observe the eclipse in 1914.

Besides those who have been removed by death from the roll of the Society, there are some who have lost their lives while fighting for their country, whom we had hoped at no distant date to welcome into the Society and thereby mark our appreciation of the services they had rendered to science.

I can mention but two names: Mr. GEOFFREY SMITH, whose contributions to biology had marked him out as one to whom that science would owe much, and Prof. McClaren, the author of valuable investigations on the difficult problem of the Equipartition of Energy. Of these and other young men of science fallen in the war we may say in the words of Dr. Montague James, "Many and diverse were the hopes and expectations we had formed for them, but every one of these has been surpassed by the event. They have all been found capable of making the greatest denial of self that men can make; they paid away their own life that the life of their fellows might be happy."

During the past year the work of the Society as a body as well as that of its members individually has been concentrated on problems connected with the war.

The Physiological Committee has done important work on the food supply of the country.

The Engineering Committee have been busy with applications of their science to Naval and Military purposes; the Chemical Committee with the preparation of substances of which the supply has been interrupted by the war.

The Society has been entrusted with the difficult task of selecting those chemists whose services could be employed more advantageously in chemical work than in active service at the front. The Society has also compiled a register of trained scientific workers which has proved exceedingly useful in finding men competent to attack the many scientific investigations demanded by the war.

The National Physical Laboratory has during the past year been working at high pressure on investigations of great importance to the country at this crisis.

Apart from the work of the Sociéty as a body, very many of our Fellows have since the war began been engaged with investigations directly connected with it. The resources of almost every laboratory in the country have been employed on work intended to be of service to our Army or Navy. The number and nature of these researches is striking evidence of the extent to which even the most recondite branches of science can find application in modern warfare. Many of these investigations are of extreme difficulty, effects have to be detected amidst the noise of a battleship or the din of an engagement which it would formerly have been thought somewhat of a feat to measure in the quiet of a laboratory. The work, too, has to be done as a race against time, and when, from conditions arising from the war, apparatus and assistance are very difficult to obtain. I think the experience we have

gained in the past two years points very strongly to the desirability of having as part of the permanent establishment of both the Army and Navy, special laboratories, properly equipped and in close touch with the services, whose work should be the discovery and development of applications of Physical, Chemical, and Engineering Science for Military and Naval purposes. The cost of modern warfare is so great that the expense of these laboratories over long periods of peace would be more than recouped if they succeeded in saving a single battleship or ensured the success of an attack.

Second only in importance to questions connected with the successful prosecution of the war is the question how best to remedy those defects in our industrial organisation and educational methods which have been revealed under the stress to which the country has been exposed by the war. Many of these are closely connected with science but they are no less closely connected with economic and political considerations. For example, we have been taught by bitter experience that it is not safe to have regard to nothing but money profit in developing the industries of the country, we have to recognise that the possibility of the country being attacked by bitter and powerful enemies is one that cannot be lost sight of, and that when this happens it makes a great deal of difference to the strength of a country whether the energies of its people have been directed to production or to importing and selling on commission the productions of the enemy. We cannot, however, produce everything, and the selection of what we should produce is a vital one and depends as much upon economic and political considerations as upon purely scientific ones.

It is, I think, important in any consideration of this subject to remember the duality of this question, for the kind of scientific training required for those who are to develop these industries will depend upon the industries selected, and we must arrange this training so that it is appropriate to the industrial conditions—it is no use making ammunition if it will not fit the guns. It may, for example, require some changes in our industrial organisation to get the full benefit of the application of scientific research to our industries. There are probably but few firms in the country but would benefit from an increase in the research work they undertake, and this not only from the commercial value of the results obtained, but from the spirit of vigour, youthfulness, and independence which successful research brings in its train.

We must remember, however, that many of the most important lines of research in applied science may require such an expenditure of time and money as to be beyond the powers of any firms which have not quite exceptional wealth and resources, and even with these, the English impatience at any

expenditure which does not show a clear prospect of an early return, together with a wide prevalence of a lack of intensity of faith in the certainty of obtaining any results by the application of scientific methods, would make it difficult for even a powerful company to carry its shareholders with it in undertaking a research which might take many years' labour and great expenditure before any profit was obtained. It would seem that for research to have its full effect on our industries, associations must be formed among those engaged in any particular industry—developments of the idea which is embodied in the old Trade Guilds and City Companies—and that one of the primary functions of these associations should be research for the benefit of the industry, carried out in Institutes connected with the association. There are fortunately indications that the formation of associations is already under consideration in certain industries.

We must be careful, however, and I think this might be regarded by the Royal Society as one of its most important duties, that the badly needed increase in research in applied science is not accompanied by any slackening off in research in pure science, that is, research made without the idea of commercial application, but solely with the view of increasing our knowledge of the laws of nature. Even from the crudest utilitarian point of view, nothing could be more foolish than the neglect of pure science, for most of the great changes that have revolutionised or created great industries have come from discoveries made without any thought of their practical applica-It may seem paradoxical, but I think it is true, that, the more remote an investigation appears to be from the regions which appear most promising from the point of view of the established industrial practice of the country, the greater are the effects it may produce on the industries of the country. Applied science may lead to reform in our industry, it is to pure science we must look for revolutions. It is not the improvement of old ideas, but rather the discovery of new ones, which produces the most revolutionary effects.

It is often said that in this country we have been slow in seeing the possibilities, for industrial purposes, of new discoveries in pure science, and I am afraid there is some truth in the accusation. One of the reasons for this is, I think, that there has not in the past been sufficient co-operation between the workers in pure science and those who are responsible for the control of our great industries. By such co-operation I do not mean that the physicist or chemist should work himself at any industrial application of his discoveries; he is wanted for other things, and there are others familiar with the industry who could work out the application far more effectively. What I do mean is that, if possible application of a discovery occurred, say to a physicist, it should be easy for him to go to the proper quarters and be able

to point out the possibility to those best able to carry it into effect. One of the objects of the newly formed Conjoint Board of Scientific Societies is to promote closer union between workers in pure and applied science.

One difficulty connected with these plans for reconstruction after the war is, I am afraid, formidable. They all require a large increase in the supply of able and well trained workers. Now, where are they to come from? Already before the war the demand exceeded the supply; since the war training for the scientific professions has necessarily ceased, and many of those who had been trained have fallen. We are faced with the position that the demand will be increased when the supply is below even the normal amount. We must tap new sources of supply. The only source I can see likely to yield an adequate number is the elementary schools of the country. We must try if we cannot "comb" out, to use the word of the moment, from these schools all the boys able to profit by further training, and try to prevent them drifting into employment of secondary importance to the State. There is at present lamentable leakage between primary and secondary schools, and also from the secondary schools themselves, for which the State is, to a considerable extent, responsible. It considers with great care the kind of training to be given in our elementary schools, but when a child has been through this training it gives no guidance whatever as to how it can best be used for the service of State. We want badly some machinery for instructing people what best to do with their children after passing through the primary school. Something which will point out as simply as possible the callings open to them, the training required for these, the assistance which the State would give, if necessary, towards this training, and the opportunity for employment and remuneration after the training has been completed. We want to make the advantages of secondary education much more tangible than they are at present. The position with regard to the supply of adequately trained workers is critical, and calls for earnest and immediate attention.

I now pass on to the most gratifying part of our proceedings this afternoon, the award of the medals.

The Copley Medal is awarded to Sir James Dewar. For more than fifty years he has been indefatigable and most successful in his efforts to increase natural knowledge. In collaboration with Dr. Liveing he made long and most important series of spectroscopic investigations, which have recently been published in a collected form. His well known long continued investigations on the liquefaction and solidification of gases have been one of the most striking features of modern science. Not only has he

taught us how to liquefy gases on a large scale, but he has made notable investigations on the properties of matter at the low temperatures which can only be obtained by their use. His investigations on specific heats of elements at low temperatures, and those made with Dr. Fleming on the effects of low temperatures on the resistance of metals, have yielded most interesting and suggestive results.

Many of the most interesting and important investigations made in Physics in recent years would have been impossible but for his invention of the method of obtaining very high vacua by the use of charcoal immersed in liquid air or hydrogen.

The nation owes a debt of gratitude to Sir James Dewar for his unwearied work, which the Royal Society tries to acknowledge by awarding him the Copley Medal.

The Rumford Medal has been awarded to Prof. William Henry Bragg for his researches into the nature and property of the rays from radioactive bodies and on other kinds of ionising radiations.

His experiments on  $\alpha$ -rays threw a new light on the nature of the absorption of  $\alpha$ -rays by matter and showed that the  $\alpha$ -rays from each radioactive transformation have a definite and characteristic range depending on their initial velocity.

Lately Prof. Bragg, working in collaboration with his son, Mr. W. L. Bragg, has made most important investigations on the interference spectra of X-rays reflected from crystals; these investigations, which formed the subject of the Bakerian Lecture, 1915, have led to a method of great beauty and power for the investigation of the molecular structure of crystals, which has already yielded results of the first importance.

A Royal Medal has been awarded to Prof. Hector Munro Macdonald for his researches in Mathematical Physics.

Prof. Macdonald is the author of an important series of papers on the diffraction of electrical waves by a large spherical obstacle, a problem which is of especial importance in connection with the transmission over the earth's surface of the waves used in wireless telegraphy. He has also made a valuable contribution to the theory of Bessel's functions and has obtained results which promise to have important applications to some problems in Mathematical Physics.

His work has extended over a wide range, for, in addition to his work on electrical waves, he has made valuable contributions to Hydrodynamics, Elasticity, and Optics.

The other Royal Medal has been awarded to Dr. John Scott Haldane for the important contributions he has made to Physiology, especially on the subject of respiration. His studies of the combination of carbon monoxide with hemoglobin have been fruitful in many directions. They led him to the investigation of gas explosions in coal mines, which has had important results in the saving of life in mines. He has also studied the effect of high temperatures under varying conditions of moisture on the human body, and was the first to lay down the definite conditions under which it is possible to withstand high temperatures or to work in them.

His work shows the rare combination of a wide philosophic insight into fundamental problems with the power of applying the knowledge gained from scientific researches to the every-day needs of the community.

The Davy Medal is awarded to Henri Louis Le Chatelier, who, as the result of much investigation, introduced the Le Chatelier thermo-electric couple and inaugurated a new period in the measurement of high temperatures. In co-operation with M. Mallard he made extensive investigations on the ignition and explosion of gaseous mixtures, in which several principles of first-rate importance were established. He was one of the pioneers in micrometallurgy and one of the first to introduce exact methods and clear ideas into the science of industrial silicates. His work has been carried out in close relation to the practical application of science, and his discoveries have been of great industrial importance.

The Darwin Medal is awarded to Prof. Yves Delage for his important investigations on the development of Sponges and for his contributions to Biology and Zoology.

The Sylvester Medal is awarded to Prof. Jean Gaston Darboux, Perpetual Secretary for Mathematical Sciences to the Academy of Sciences, one of the most distinguished of contemporary French Mathematicians. He has published work of the first importance on the Theory of Surfaces, the Theory of Partial Differential Equations, Kinematics, and the Planetary Theory.

The Hughes Medal is awarded to Dr. Elihu Thompson, one of the pioneers of Electrical Engineering, for his important contributions to that subject.

Motion of Solids in Fluids when the Flow is not Irrotational.

By G. I. TAYLOR, M.A.

(Communicated by Prof. H. Lamb, F.R.S. Received April 13, 1916.)

The chief interest in the results obtained in the following pages lies in the fact that a mathematical result has been obtained concerning the motion of solids in fluids which is verified accurately when recourse is had to experiment, with real solids moving in real fluids. This is so exceptional a circumstance that it is hoped that the interest which it gives to the mathematical work will serve to extenuate, to a certain extent, the clumsiness of the methods employed.

The problem solved is two-dimensional. An infinite cylindrical body of any cross-section moves in a uniformly rotating fluid with its generators parallel to the axis of rotation. The stream lines and the reaction between the solid and the fluid are found.

Suppose that a stream function  $\psi'$  has been found which represents the irrotational motion of an incompressible fluid when a cylindrical solid (or several cylindrical solids) of the required cross-section is moved in an assigned manner starting from rest in a fluid which has a given boundary or has a given irrotational motion at infinity.  $\psi'$  is a function of x and y, the co-ordinates of a point in a plane perpendicular to the axis of rotation, and o t, the time.

Since the motion is irrotational  $\psi'$  satisfies the relation  $\nabla^2 \psi' = 0$  everywhere, and  $-\partial \psi'/\partial s = V_n'$  at the solid boundaries, where  $V_n'$  represents the velocity normal to the boundary of a point on the surface of a cylindrical solid moving in the fluid, and  $\partial \psi'/\partial s$  represents the rate of change in  $\psi'$  measured in a direction along the solid boundary. These, together with the conditions at infinity, if the fluid is unenclosed, are the necessary and sufficient conditions for determining  $\psi'$ . The components of velocity of the fluid are then

$$u' = -\partial \psi'/\partial y$$
 and  $v' = \partial \psi'/\partial x$ .

Now consider the function

$$\psi = \psi' + \frac{1}{2}\omega (x^2 + y^2), \tag{1}$$

where  $\omega$  is a constant both in regard to space and to time. It satisfies the dynamical equations of motion,  $D/Dt(\nabla^2\psi) = 0$  for  $\nabla^2\psi = 2\omega$ , which is constant; and it is the stream function of the fluid motion obtained when the whole system represented by  $\psi'$  is rotated with uniform angular velocity  $\omega$ 

about the origin. The boundary conditions of the rotating system are evidently satisfied if the cylindrical solids move relative to the rotating system in the same way that they moved relative to fixed axes in the case of the motion represented by  $\psi'$ . Hence it appears that the system consisting of the cylindrical solids and the fluid in which they move may be rotated uniformly without affecting the motion of the fluid relative to the rotating system, provided the cylinders are constrained to move, relative to the rotating system, in the same way that they moved, relative to fixed axes, when the system was not rotating.\* If, however, the solids are free to move under the action of their own inertia and of the pressure of the fluid, the rotation will make a considerable difference to the relative motion of the solids and the fluid. It therefore becomes important to find the pressure at any point.

Let p' be the pressure at the point (x, y) in the irrotational case, and let p be the pressure when the whole system is rotated.

The equations for p and p' are

$$-\frac{1}{\rho}\frac{\partial p'}{\partial x} = \frac{\partial u'}{\partial t} + u'\frac{\partial u'}{\partial x} + v'\frac{\partial u'}{\partial y} 
-\frac{1}{\rho}\frac{\partial p'}{\partial y} = \frac{\partial v'}{\partial t} + u'\frac{\partial v'}{\partial x} + v'\frac{\partial v'}{\partial y}$$
(2)

$$-\frac{1}{\rho}\frac{\partial p}{\partial x} = \frac{\delta u}{\delta t} + u\frac{\partial u}{\partial x} + v\frac{\partial u}{\partial y} - \frac{1}{\rho}\frac{\partial p}{\partial y} = \frac{\delta v}{\delta t} + u\frac{\partial v}{\partial x} + v\frac{\partial v}{\partial y},$$
(3)

where u and v are the components of velocity in the rotational motion.

The symbol  $\delta u/\delta t$  has been used to represent the rate of change, at a point fixed in space, in the component of velocity parallel to a fixed direction which momentarily coincides with the axis of x.

This is not the same thing as  $\partial u/\partial t$ . Since u may be regarded as being known in terms of the co-ordinates (x and y), referred to rotating axes, and t the time,  $\partial u/\partial t$  represents the rate of change in the component of the velocity of the fluid which is parallel to the rotating axis of x at a point which moves with the axes. It is evident that  $\partial u/\partial t = \partial u'/\partial t$  and  $\partial v/\partial t = \partial v'/\partial t$ .

To find the value of  $\delta u/\delta t$  and  $\delta v/\delta t$ , consider the rate of change, at a point fixed in space, in the component of velocity parallel to a fixed direction which momentarily makes an angle  $\beta$  with the axis of x.

\* It will be shown later that this proposition cannot be extended to the case of the three-dimensional motion.

The component of the velocity of the fluid parallel to this direction is  $u \cos \beta + v \sin \beta$ .

After a short interval of time,  $\delta t$ , the co-ordinates of the fixed point relative to the moving axes are

$$x + \omega y \delta t$$
 and  $y - \omega x \delta t$ .

The components of velocity parallel to the rotating axes (which now make an angle  $\omega \delta t$  with their previous positions) are

$$u + \left(\frac{\partial u}{\partial t} + \omega y \frac{\partial u}{\partial x} - \omega x \frac{\partial u}{\partial y}\right) \delta t \quad \text{and} \quad v + \left(\frac{\partial v}{\partial t} + \omega y \frac{\partial v}{\partial x} - \omega x \frac{\partial v}{\partial y}\right) \delta t.$$

The component of velocity parallel to the fixed direction is therefore

$$\left[u + \left(\frac{\partial u}{\partial t} + \omega y \frac{\partial u}{\partial x} - \omega x \frac{\partial u}{\partial y}\right) \delta t\right] \cos(\beta - \omega \delta t) + \left[v + \left(\frac{\partial v}{\partial t} + \omega y \frac{\partial v}{\partial x} - \omega x \frac{\partial v}{\partial y}\right) \delta t\right] \sin(\beta - \omega \delta t).$$

The rate of change in velocity parallel to the fixed direction is therefore

$$\left(\frac{\partial u}{\partial t} + \omega y \frac{\partial u}{\partial x} - \omega x \frac{\partial u}{\partial y} - \omega v\right) \cos \beta + \left(\frac{\partial v}{\partial t} + \omega y \frac{\partial v}{\partial x} - \omega x \frac{\partial v}{\partial y} + \omega u\right) \sin \beta.$$

Putting  $\beta = 0$  we find

$$\frac{\delta u}{\delta t} = \frac{\partial u}{\partial t} + \omega y \frac{\partial u}{\partial x} - \omega x \frac{\partial u}{\partial y} - \omega v$$

and putting  $\beta = \frac{1}{2}\pi$ ,

$$\frac{\delta v}{\delta t} = \frac{\partial v}{\partial t} + \omega y \frac{\partial v}{\partial x} - \omega x \frac{\partial v}{\partial y} + \omega u.$$

Substituting these values in (3), subtracting equations (2) and substituting for u and v, it will be found that

$$-\frac{1}{\rho}\frac{\partial}{\partial x}(p-p') = -\omega^2 x - 2\omega v' \quad \text{and} \quad -\frac{1}{\rho}\frac{\partial}{\partial y}(p-p') = -\omega^2 y + 2\omega u'.$$

These equations may be integrated in the form

$$(p-p')/\rho = \frac{1}{2}\omega^2(x^2+y^2) + 2\omega\psi'. \tag{4}$$

At this stage it is easy to prove that the proposition proved on p. 100 cannot be extended to the case of three-dimensional motion.

Let u', v', w' be the components of the velocity of a fluid in irrotational motion. Suppose that the motion defined by

$$u = u' - \omega y, \quad v = v' + \omega y, \quad w = w',$$

is possible.

Proceeding as before, it will be found that the pressure equations can be reduced to

$$-\frac{1}{\rho}\frac{\partial}{\partial x}(p-p') = -\omega^2 x - 2\omega v',$$

$$-\frac{1}{\rho}\frac{\partial}{\partial y}(p-p') = -\omega^2 y + 2\omega u',$$

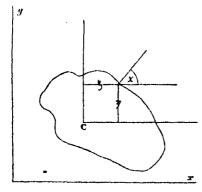
$$-\frac{1}{\rho}\frac{\partial}{\partial z}(p-p') = 0.$$

These are not consistent unless u' and v' are independent of z; that is, unless the motion is two-dimensional.

Let us now apply (4) to find the resultant force and couple which the fluid pressure exerts on a solid moving in a rotating fluid,

Let  $F_{x'}$ ,  $F_{y'}$ , and G' be the resultant forces and couple due to fluid pressure on the solid in the case when the system is not rotating.  $F_{x'}$  and  $F_{y'}$  are supposed to act at the centre of gravity C of the area of the cross-section of the solid. Let  $F_{x}$ ,  $F_{y'}$ , and G be the corresponding quantities in the case when the system is rotating.

If  $\chi$  represents the angle between the normal to the surface of the solid and the axis of x, then



$$F_{x}-F_{x'} = -\int (p-p')\cos\chi ds,$$

$$F_{y}-F_{y'} = -\int_{s} (p-p')\sin\chi ds,$$

$$G-G' = \int_{s} (p-p')(\eta\cos\chi - \xi\sin\chi) ds,$$

where  $\xi$  and  $\eta$  are the co-ordinates of a point on the surface referred to axes parallel to the axes of x and y, and passing through C; and the integrals are

taken round the surface of the solid. Substituting the value of p-p' given by (4) these may be integrated.

Thus

$$-\frac{\mathbf{F}_z - \mathbf{F}_{z'}}{\rho} = \frac{1}{\rho} \int_{s} (p - p') \cos \chi ds = \frac{\omega^2}{2} \int_{s} (x^2 + y^2) \cos \chi ds + 2\omega \int_{s} \psi' \cos \chi ds. \quad (5)$$

Now  $\int_s y^2 \cos \chi ds$  vanishes since  $\cos \chi ds = dy$ . Also  $\frac{\omega^2}{2} \int_s x^2 \cos \chi ds = \omega^2 A x_0$ ,

where A is the area of cross-section of the solid, and  $(x_0, y_0)$  are the coordinates of its centroid.

 $2\omega \int \psi' \cos \chi ds$  may be integrated by parts. It then becomes

$$-2\omega \int_{s} y \frac{d\psi'}{ds} ds = -2\omega \int_{s} (y_{0} + \eta) \frac{d\psi'}{ds} ds = -2\omega \int_{s} \eta \frac{d\psi'}{ds} ds, \qquad (6)$$

since  $\int y_0 \frac{d\psi'}{ds} ds$  evidently vanishes.

Now  $-\partial \psi'/\partial s$  represents the velocity of the fluid normal to the surface of the solid. The boundary condition which must be satisfied by  $\psi'$  is

$$-\partial \psi'/\partial s = (\dot{x}_0 - \Omega \eta)\cos \chi + (\dot{y}_0 + \Omega \xi)\sin \chi,$$

where  $\Omega$  is the angular velocity of the body.

Substituting in (6) and remembering that  $\cos \chi ds = d\eta$  and  $\sin \chi ds = -d\xi$ , it will be found that

$$2\omega \int_{s} \psi' \cos \chi ds = 2\omega \int_{s} \eta \left(\dot{x_0} - \Omega \eta\right) d\eta - 2\omega \int_{s} (\dot{y}_0 + \Omega \xi) \eta d\xi.$$

The first of these integrals vanishes and the second may be written

$$-2\omega\dot{y}_0\int_{s}\eta d\xi-2\omega\Omega\int_{s}\eta\xi d\xi,$$

Now  $\int_s \eta d\xi = -A$  and  $\int_s \eta \xi d\xi = 0$ , since C is the centroid of the area of cross-section.

Hence from (5) 
$$-(\mathbf{F}_x - \mathbf{F}_{x'})/\rho = \omega^2 \mathbf{A} x_0 + 2\omega \mathbf{A} \dot{y}_0.$$

Similarly it will be found that

$$-(\mathbf{F}_{y}-\mathbf{F}_{y}')/\rho = \omega^{2}\mathbf{A}y_{0}-2\omega\mathbf{A}\dot{x}_{0}.$$

It will be noticed that  $\omega^2 A x_0$  and  $\omega^2 A y_0$  are the components of a force  $\omega^2 A R$  acting radially, R being the distance of C from the centre of rotation. Also  $2 \omega A \dot{y}_0$  and  $-2 \omega A \dot{x}_0$  are the components of a force  $2 \omega A Q$  acting at right angles to the direction of motion of C relative to the rotating axes, Q being the relative velocity of C.

Now consider the couple G-G' due to the rotation

$$\frac{\mathbf{G} - \mathbf{G'}}{\rho} = \int_{s} \frac{p - p'}{\rho} (\eta \, d\eta + \xi \, d\xi).$$

Substituting from (4),

$$G - G' = \frac{\omega^2}{2} \int_{s} \{ (x_0 + \xi)^2 + (y_0 + \eta)^2 \} (\eta d\eta + \xi d\xi) + 2 \omega \int_{s} \psi' (\eta d\eta + \xi d\xi).$$

Neglecting all terms which contain only powers of  $\xi$  or of  $\eta^*$  and integrating the second integral by parts, this becomes

$$\frac{G-G'}{\rho} = \frac{\omega^2}{2} \left[ 2x_0 \int_s \xi \eta \, d\eta + 2y_0 \int_s \eta \xi \, d\xi + \int_s \xi^2 \eta \, d\eta + \int_s \eta^2 \xi \, d\xi \right]$$

$$-2\omega \int_s \frac{\xi^2 + \eta^2}{2} \frac{d\psi'}{ds} \, ds.$$
Now
$$\int_s \xi \eta \, d\eta = \int_s \eta \xi \, d\xi = 0,$$
and
$$\int_s \xi^2 \eta \, d\eta + \int_s \eta^2 \xi \, d\xi = \frac{1}{2} \int_s d(\xi^2 \eta^2) = 0;$$

and

also since

$$\int_{s} \xi^{2} \eta \, d\eta + \int_{s} \eta^{2} \xi \, d\xi = \frac{1}{2} \int_{s} d(\xi^{2} \eta^{2}) = 0;$$
$$-(\partial \psi'/\partial s) \, ds = (\dot{x}_{0} - \Omega \eta) \, d\eta + (\dot{y}_{0} + \Omega \xi) \, d\xi,$$

 $(G-G')/\rho$  reduces to

$$2\omega \left[\dot{x}_0 \int_{\frac{1}{2}}^{\frac{1}{2}} \xi^2 d\eta - \dot{y}_0 \int_{\frac{1}{2}}^{\frac{1}{2}} \eta^2 d\xi - \Omega \int_{\frac{1}{2}}^{\frac{1}{2}} \xi^2 \eta d\eta - \Omega \int_{\frac{1}{2}}^{\frac{1}{2}} \eta^2 \xi d\xi \right] = 0.$$

The forces due to fluid pressure, which act on a body moving in an assigned manner in a rotating fluid, may therefore be regarded as being made up as follows:—

- (1) The forces  $F_{z}$ ,  $F_{y}$ , and the couple G' which would act on the body if it moved in the same way relatively to the fluid at rest.
- (2) A force equivalent to  $\rho\omega^2AR$  acting towards the centre of rotation through C.
- (3) A force  $2\rho\omega AQ$  acting at C in a direction perpendicular to the relative motion of C and the rotating axes, and directed to the left if the rotation of the fluid is anti-clockwise.

We can therefore solve any problem on the motion of cylindrical solids in a rotating fluid if we can obtain a solution of a similar problem respecting the motion of the solids in a fluid at rest.

Now, consider the forces and the couple which it is necessary to apply to a solid body of mass M, in order that it may move in an assigned manner relatively to rotating axes. Suppose that a force F' and a couple G' must be applied at its centre of gravity, in order that it may move in the assigned manner relatively to fixed axes. The additional force which it is necessary to apply when the system is rotating uniformly with angular velocity  $\omega$  may be shown to consist of a force  $2M\omega Q$  perpendicular to the direction of the velocity Q of the centre of gravity relative to the rotating system, together with a force  $M\omega^2R$  acting through the centre of gravity towards the centre of rotation.

<sup>\*</sup> For they vanish when integrated round a closed contour.

It will be noticed that, if the position of the centre of gravity of the solid coincides with the centroid of its cross-section, and if the mass per unit length of the solid is equal to  $\rho$ A, that is to say, if the mass and the centre of gravity of the solid are the same as those of the fluid displaced, then these forces are the same as those which act on the solid, owing to the additional pressures in the fluid due to its rotation.

These considerations lead to the conclusion that, if a solid of the same density as the fluid be moved along a certain path by certain assigned external forces, then a uniform rotation of the whole system, including the external force, makes no difference to the path which the solid pursues relative to the system.

This theorem applies only to the case of two-dimensional motion. In the case of a finite cylinder, for instance, it seems almost obvious that the pressures due to the rotation must fall off towards its ends. It is natural to suppose, therefore, that the reaction of the fluid would not be sufficient to hold a finite cylinder in its path when the whole system is rotated.

The case of a sphere moving in a rotating fluid presents considerable mathematical difficulties, but the initial motion has been investigated by Mr. J. Proudman, who has kindly consented to allow the author to make use of his results, though they are not yet published.\* He finds that, if a sphere of volume V starts from rest in the rotating fluid and moves with uniform velocity along a straight line relative to the rotating system, it is acted on initially by a force  $\nabla \rho \omega^2 R$  directed towards the centre of the rotation (which is at a distance R from the centre of the sphere) and by a force  $\frac{1}{2}\nabla\rho Q\omega$  acting in a direction perpendicular to its path. But in order that a sphere of the same density as the fluid, that is, one whose mass is  $\nabla \rho$ , may move along a straight path relative to the rotating system, it must be acted on by a force  $\nabla \rho \omega^2 R$  directed towards the centre of rotation and by a force  $2\nabla \rho \omega Q$  perpendicular to its path.

The forces due to fluid pressure are not sufficient to supply the second of these. If, therefore, the sphere were drawn through the rotating fluid by means of a string, it would not move in the direction the string was pulling it, but would be deflected to the left if the fluid were rotating clockwise, and to the right if were rotating anticlockwise. On the other hand, if a cylinder of the same density were drawn through the rotating fluid, the force necessary to hold it in its straight path would be supplied by the fluid pressure. The cylinder would therefore move straight through the fluid in the direction the string was pulling it.

<sup>\*</sup> Since the above was written Mr. Proudman has published his results. They appeared in 'Roy. Soc. Proc.,' A, vol. 92, pp. 408-424 (1916).

These conclusions have been tested and completely verified by means of experiments made by the author in the Cavendish Laboratory with water in a rotating tank.

Experiments made with a Rotating Tank of Water.

A glass tank full of water was mounted so that it could be rotated about a vertical axis at various speeds by means of an electric motor. The speeds varied from 2 to 6 seconds per revolution. Two bodies were prepared, one cylindrical and the other spherical. The former consisted of a piece of thin-walled brass tube about 6 in. × \frac{3}{2} in stopped at the end with waxed cork, while the other was a spherical glass bulb. They were weighted until they would fall very slowly through water, and the positions of the weights were adjusted till they would stay almost at rest in any position in the water. The centres of gravity of the bodies were then coincident with the centres of gravity of the water displaced by them.

A simple mechanism was next devised to tow them through the tank from one end to the other. It consisted of a wood pulley about 4 inches in diameter mounted on a vertical spindle which was driven into a wood bridge, fixed to the tank over the middle of it. This spindle coincided with the axis of rotation of the tank. Cotton was then wound round the pulley, passed through some small rings screwed into a board fixed to one end of the tank, and led horizontally along the tank to the cylinder or sphere, which was fixed at the other end.

The body was held in a holder while the tank and water were being brought to a state of uniform rotation. A device was arranged so that the holder could release the body and at the same moment the wood pulley on which the cotton was wound could be fixed in space. As the tank was then rotating round the pulley the cotton wound up round it, and pulled the bodies along the middle of the tank from one end to the other.

Result.—It was found that the cylinder moved straight through the middle of the tank. Even when the tank was rotating very rapidly the cylinder always passed over the central line. The sphere, however, was violently deviated to the left (the tank was rotating clockwise). When the tank was rotated quite slowly, about once in 6 seconds, the sphere would not quite touch the side, though it never came up to the stop at the other end from a direction less than 45° away from the central line. When the tank rotated more rapidly the complete path could never be seen, because the sphere always hit the side of the tank before it had gone more than a few inches in the direction along which the cotton was trying to pull it. After striking the side of the tank the sphere would follow the side along, touching all the time,

till it got to a position close to the other end where the string was pulling in a direction making an angle of about 50° with the side of the tank. It would leave the side and approach the point towards which the cotton was pulling it along a curved path.

The accuracy with which the experiments just described verify the hydrodynamical theory of rotating fluids is at first sight most surprising. Besides the fact that there is apparently no other case in which experiments made with real solids moving in real fluids agree with the predictions of hydrodynamics, it is known that the stream lines of a real fluid round a circular cylinder in particular bear no resemblance to the stream lines used in the ordinary hydrodynamical theory. It will be noticed, however, that in order that there may be agreement between theory and experiment in the particular respect to which attention has been drawn, it is unnecessary that the actual flow pattern shall be the same as the flow pattern contemplated in the ordinary hydrodynamical theory. All that is necessary is that the flow pattern in the case of the cylinder shall be two-dimensional, while that in the case of the sphere shall be three-dimensional.

## Experiments with Vortex Rings in a Rotating Fluid.

The theory explained on p. 105 leads to the conclusion that if a homogeneous solid, which is not cylindrical, be projected in a rotating fluid of the same density as itself it will be deviated, to the left if the rotation is clockwise, and to the right if the rotation is anti-clockwise, of the path it would pursue through the fluid if the whole system were not rotating. Now, a vortex ring affects the fluid round it in much the same way as a solid ring of the same dimensions as the cyclic portion of the flow system. If it is projected through a fluid at rest it travels along a straight line. We should expect, therefore, that if a vortex ring were projected through a rotating fluid it would follow a curved path relative to the fluid, being deviated to the left if the fluid were rotating clockwise.

This conclusion was tested experimentally and found to be correct. A small vortex box with a rubber top and a circular hole in the side was made. This was filled with a solution of fluoresceïn and placed in one end of the tank, which was filled with water and held fixed. On striking the rubber lightly a vortex ring was produced which travelled straight down the tank and struck the middle of the opposite end.

The same experiment was repeated when the tank and vortex box were rotating. On tapping the box, rings started out in the same direction as before, but were deflected in a curved path, so that they hit the side instead of the end of the tank. By tapping the box quite lightly and rotating the

tank fairly rapidly the rings could be made to turn in such small circles that they came round and struck the vortex box again without touching the side of the tank on the way. They would, in fact, turn in a circle whose diameter was only about four times the diameter of the rings.

It was pointed out by Dr. F. W. Aston, to whom the writer was showing this experiment, that the rings appeared to remain parallel to a plane fixed in space, while the rest of the fluid rotated. He suggested that the gyroscopic action prevented the ring from being deviated from this plane, and that in order that the ring might move relative to the fluid in a direction perpendicular to its plane it would have to move through the fluid along a curved path.

Motion of a Circular Cylinder in a Fluid which has a Steady Rotational Motion at Infinity but does not Necessarily Rotate as a Whole.

The results given in the rest of this paper have no immediate practical interest. The author entered on the investigation with a view to getting an idea of how the instability which is known to exist in a uniformly shearing laminar flow would be likely to manifest itself, and to find out whether the characteristics of the motion of solids in rotating fluids, which have been discussed in the first part of this paper, have any counterpart in the case of solids moving a fluid whose undisturbed motion is a uniform laminar flow.

The problem of finding the motion of a circular cylinder in a rotationally moving fluid divides itself naturally into two parts, that of finding the stream function for a given motion of the cylinder, and that of finding the force which the pressure associated with that stream function exerts on the cylinder. The stream function for a certain type of rotational flow in which the vorticity is uniform will now be found.

Let  $(r, \theta)$  be the polar co-ordinates of a point referred to axes through the centre of the cylinder, and let  $(x_0, y_0)$  be the co-ordinates of the centre of the cylinder referred to fixed axes, so that the equation  $\theta = 0$  represents a line parallel to the axis of x at a distance  $y_0$  from it.

Consider the stream function

$$\psi = \frac{1}{2}\zeta r^{2} + (Ar + B/r)\cos\theta + (Cr + D/r)\sin\theta + (Er^{2} + F/r^{2})\cos 2\theta + (Gr^{2} + H/r^{2})\sin 2\theta.$$
 (7)

It satisfies the equation  $\nabla^2 \psi = 2 \zeta$  everywhere.

If, therefore, the constants A, B, C, etc., be so chosen that the boundary condition

$$\partial \psi / r \partial \theta + \dot{x}_0 \cos \theta + \dot{y}_0 \sin \theta = 0 \tag{8}$$

is satisfied where r = a, a being the radius of the cylinder, then  $\psi$  is the

stream function which represents the motion of a fluid which, if the cylinder were removed, would be moving in accordance with the velocities given by the stream function.

$$\psi_1 = \zeta r^2 / 2 + \operatorname{Ar} \cos \theta + \operatorname{Cr} \sin \theta + \operatorname{Er}^2 \cos 2\theta + \operatorname{Gr}^2 \sin 2\theta. \tag{9}$$

Now (8) must be satisfied for all values of  $\theta$ ; hence we may equate coefficients of  $\cos \theta$ ,  $\sin \theta$ ,  $\cos 2\theta$ , and  $\sin 2\theta$ , separately to zero. In this way the following relations between the constants are determined:—

$$A + B/a^2 - \dot{y}_0 = 0$$
,  $C + D/a^2 + \dot{x}_0 = 0$ ,  $Ea + F/a^3 = 0$ ,  $Ga + H/a^3 = 0$ . (10)

It will be noticed that  $\psi_1$ , the stream function of the fluid before the introduction of the cylinder, is expressed in terms of co-ordinates referred to moving axes. In order to find the motion of a cylinder in a fluid whose undisturbed motion before the introduction of the cylinder is known with reference to fixed axes, we must transform (9) so as to give  $\psi_1$  in terms of co-ordinates x and y referred to the fixed axes used to fix the position of the cylinder. The transformation is performed by putting

$$r\cos\theta = x - x_0$$
,  $r\sin\theta = y - y_0$ .

 $\psi_1$  then becomes

$$\frac{1}{2}\xi\{(x-x_0)^2+(y-y_0)^2\}+A(x-x_0)+C(y-y_0) + E\{(x-x_0)^2-(y-y_0)^2\}+2G(x-x_0)(y-y_0).$$
(11)

If the motion of the fluid before the introduction of the cylinder be given by the function

$$\psi_1 = \frac{1}{2} \zeta(x^2 + y^2) + A'x + C'y + E'(x^2 - y^2) + 2G'xy, \tag{12}$$

where A', C', E', G' are given constants, we find, by equating coefficients of x, y,  $x^2$ , xy,  $y^2$  in (11) and (12), the following relations determining A, C, E, G, in terms of A', C', E', G',  $x_0$  and  $y_0$ ,

$$-\zeta x_0 + \mathbf{A} - 2\mathbf{E} x_0 - 2\mathbf{G} y_0 = \mathbf{A}', \qquad -\zeta y_0 + \mathbf{C} + 2\mathbf{E} y_0 - 2\mathbf{G} x_0 = \mathbf{C}',$$

$$\mathbf{E} = \mathbf{E}', \qquad \mathbf{G} = \mathbf{G}.'$$
(13)

Solving (10) and (13) we obtain the following values of A, B, C, I), E, F, G, H,

$$A = A' + \zeta x_0 + 2E' x_0 + 2G' y_0,$$

$$B = -\alpha^2 (-\dot{y}_0 + A' + \zeta x_0 + 2E' x_0 + 2G' y_0),$$

$$C = C' + \zeta y_0 - 2E' y_0 + 2G' x_0,$$

$$D = -\alpha^2 (\dot{x}_0 + c' + \zeta y_0 - 2E' y_0 + 2G' x_0),$$

$$E = E', \quad F = -E' \alpha^4,$$

$$G = G', \quad H = -G' \alpha^4.$$
(14)

Hence the stream function is obtained for the motion of a cylinder in a fluid whose undisturbed motion may be expressed by a stream function of the form  $\psi_1$ . The two particular cases which are of the greatest interest are those of uniform rotation, for which  $\psi_1 = \frac{1}{2} \omega (x^2 + y^2)$ , and uniformly shearing laminar flow, for which  $\psi_1 = -\frac{1}{2} \alpha y^2$ ,  $\alpha$  being the rate of shear. Before discussing these cases, however, it is necessary to find an expression in terms of  $\psi$  for the force on the cylinder.

In general there does not appear to be a simple pressure integral like Bernouilli's for the case of irrotational motion, or the expression given in equation (4) for the pressure in a rotating fluid. It is necessary to go back to the original equations of motion of the fluid.

If the rate of change in pressure along a direction which makes an angle  $\chi$  with the axis of x be represented by the symbol  $dp/ds_{\chi}$ ,  $ds_{\chi}$  representing an element of length in the direction  $\chi$ , then the equation of motion is

$$-\frac{1}{\rho}\,\frac{dp}{ds_{x}} = \frac{D}{Dt}(v_{x}),$$

where  $v_{\chi}$  represents the component of velocity of the fluid in the direction  $\chi$ . Its value may be found in terms of  $\psi$  by the equation

$$v_{\chi} = \partial \psi / \partial r \cdot \sin(\chi - \theta) - \partial \psi / r \partial \theta \cdot \cos(\chi - \theta).$$
 (15)

Now  $\frac{\mathbf{D}}{\mathbf{D}t}(v)$  may be written

$$\frac{\delta v_{x}}{\delta t} - \frac{\partial \psi}{r \partial \theta} \frac{\partial}{\partial r} (v_{x}) + \frac{\partial \psi}{\partial r} \frac{\partial}{r \partial \theta} (v_{x}), \tag{16}$$

where  $\delta v_x/\delta t$  represents, as before, the rate of change in  $v_x$  at a point fixed in space.

If  $\delta r$ ,  $\delta \theta$  are the changes in the co-ordinates of a fixed point in time  $\delta t$ ,

$$\frac{\delta v_x}{\delta t} = \frac{\partial v_x}{\partial t} + \frac{\partial v_x}{\partial \theta} \frac{\delta \theta}{\delta t} + \frac{\partial v_x}{\partial r} \frac{\delta r}{\delta t},\tag{17}$$

where  $\partial v_{\chi}/\partial t$  represents the rate of change in  $v_{\chi}$  at a point fixed relative to the moving axes. The value of  $\partial v_{\chi}/\partial t$  may be obtained by differentiating the expression (15) with respect to time, which occurs in all terms which contain  $x_0$ ,  $y_0$ ,  $\dot{x}_0$  or  $\dot{y}_0$ .

The values of  $\delta r$  and  $\delta \theta$  may be found by resolving the velocity of c, the centre of the cylinder, along and perpendicular to r.

Thus

 $\delta r = -(\dot{x}_0 \cos \theta + \dot{y}_0 \sin \theta) \, \delta t, \qquad r \, \delta \theta = (\dot{x}_0 \sin \theta - \dot{y} \cos \theta) \, \delta t \,;$  substituting in (17),

$$\frac{\delta v_{x}}{\delta t} = \frac{\partial v_{x}}{\partial t} + (\dot{x}_{0} \sin \theta - \dot{y}_{0} \cos \theta) \frac{\partial v_{x}}{\partial \theta} - (\dot{x}_{0} \cos \theta + \dot{y}_{0} \sin \theta) \frac{\partial v_{x}}{\partial r};$$

substituting this in (16),

$$\begin{split} -\frac{1}{\rho}\frac{\partial p}{\partial s_{\chi}} &= \frac{\mathbf{D}}{\mathbf{D}t}\left(v_{\chi}\right) = \frac{\partial v_{\chi}}{\partial t} - \left(\frac{\partial \Psi}{r\partial \theta} + \dot{x}_{0}\cos\theta + \dot{y}_{0}\sin\theta\right)\frac{\partial v_{\chi}}{\partial r} \\ &+ \left(\frac{\partial \Psi}{\partial r} + \dot{x}_{0}\sin\theta - \dot{y}_{0}\cos\theta\right)\frac{\partial v_{\chi}}{r\partial \theta}. \end{split}$$

Now  $-\partial \psi/r\partial \theta - \dot{x_0}\cos \theta - \dot{y_0}\sin \theta$  represents the component, normal to the surface, of the relative velocity of the fluid and the cylinder. It must therefore vanish.

Hence 
$$-\frac{1}{\rho}\frac{\partial p}{\partial s_x} = \frac{\partial v_x}{\partial t} + \left(\frac{\partial \psi}{\partial r} + \dot{x}_0 \sin \theta - \dot{y}_0 \cos \theta\right) \frac{\partial v_x}{\partial \theta}$$

and substituting for  $v_x$  from (15),

$$-\frac{1}{\rho}\frac{\partial p}{\partial s} = \sin\left(\chi - \theta\right) \left[ \frac{\partial^{2} \psi}{\partial r \partial t} + \left( \frac{\partial \psi}{\partial r} + \dot{x}_{0} \sin\theta - \dot{y}_{0} \cos\theta \right) \left( \frac{\partial^{2} \psi}{r \partial r \partial \theta} - \frac{\partial \psi}{r^{2} \partial \theta} \right) \right] + \cos\left(\chi - \theta\right) \left[ -\frac{1}{r} \frac{\partial^{2} \psi}{\partial \theta} + \left( \frac{\partial \psi}{\partial r} + \dot{x}_{0} \sin\theta - \dot{y}_{0} \cos\theta \right) \left\{ -\frac{\partial \psi}{r \partial \theta} - \frac{1}{r} \frac{\partial}{r \partial \theta} \left( \frac{\partial \psi}{r \partial \theta} \right) \right\} \right].$$

If  $\chi$  be put equal to  $\frac{1}{2}\pi + \theta$ , we obtain the variation in pressure round the cylinder in the form

$$-\frac{1}{\rho} \left[ \frac{\partial p}{\partial r \partial \theta} \right]_{r=a} = \left[ \frac{\partial^2 \psi}{\partial r \partial t} + \left( \frac{\partial \psi}{\partial r} + \dot{x}_0 \sin \theta - \dot{y}_0 \cos \theta \right) \frac{\partial}{\partial r} \left( \frac{1}{r} \frac{\partial \psi}{\partial \theta} \right) \right]_{r=a}. \quad (18)$$

If  $F_x$  and  $F_y$  represent the components of the resultant force acting on the cylinder due to fluid pressure,

$$\mathbf{F}_x = -\int_0^{2\pi} p \cos \theta \, a \, d\theta, \qquad \mathbf{F}_y = -\int_0^{2\pi} p \sin \theta \, a \, d\theta.$$

These may be integrated by parts.

$$\mathbf{F}_{x}$$
 then becomes  $a^{2} \int_{0}^{2\pi} \left[ \frac{\partial p}{r \partial \theta} \right]_{r=a}^{\sin \theta} d\theta$  and  $\mathbf{F}_{y} = -a^{2} \int_{0}^{2\pi} \left[ \frac{\partial p}{r \partial \theta} \right]_{r=a}^{\cos \theta} d\theta$ . (19)

By substituting the value obtained for  $\left[\frac{\partial p}{\partial \theta}\right]_{r=a}$  in (18) we can find the force exerted by fluid pressure when the cylinder has any assigned motion for which a stream function can be found.

This method will be applied to two particular cases: In Case (1) the general motion of the fluid is one of uniform rotation. This problem has been solved already in the first part of this paper, but it seems worth while to verify the calculation. In Case (2) the general motion of the fluid is one of uniform shearing.

Case 1.—The stream function of the general motion of the fluid is

 $\psi_1 = \frac{1}{2}\omega (x^2 + y^2)$ . In this case, then,  $\zeta = \omega$  and A' = C' = E' = G' = 0. The stream function of the motion round the cylinder is

$$\psi = \omega \frac{r^2}{2} + \left\{ \omega x_0 r - \frac{a^2}{r} (-\dot{y}_0 + \omega x_0) \right\} \cos \theta + \left\{ \omega y_0 r - \frac{a^2}{r} (\dot{x}_0 + \omega y_0) \right\} \sin \theta.$$

Substituting in (18) the value of  $-\frac{1}{\rho} \left[ \frac{\partial p}{\partial \theta} \right]_{r=a}^{r}$  be found, and substituting this value in (19) it will be found that

$$-\mathbf{F}_{x} = \pi \rho \alpha^{2} (\ddot{x}_{0} + 4 \omega \dot{y}_{0} - 2 \omega^{2} x_{0}), \qquad \mathbf{F}_{y} = \pi \rho \alpha^{2} (\ddot{y}_{0} + 4 \omega \dot{x}_{0} + 2 \omega^{2} y_{0}).$$

If these expressions be transformed by the transformation

$$x_0 = R \cos(\phi + \omega t), \quad y_0 = R \sin(\phi + \omega t),$$

so that R,  $\phi$ , are the polar co-ordinates of a point referred to axes which rotate with the fluid, it will be found that the forces  $F_x$ ,  $F_y$ , may be resolved into components  $F_R$  along R, and  $F_{\phi}$  perpendicular to it where

$$\begin{split} \mathbf{F}_{\mathbf{R}} &= \pi \rho a^2 \left\{ -\ddot{\mathbf{R}} + \mathbf{R}\dot{\boldsymbol{\phi}}^2 - 2\mathbf{R}\boldsymbol{\omega}\dot{\boldsymbol{\phi}} - \mathbf{R}\boldsymbol{\omega}^2 \right\}, \\ \mathbf{F}_{\mathbf{A}} &= \pi \rho a^2 \left\{ -\mathbf{R}\ddot{\boldsymbol{\phi}} - 2\dot{\mathbf{R}}\boldsymbol{\phi} + 2\boldsymbol{\omega}\dot{\mathbf{R}} \right\}. \end{split}$$

This agrees with the results obtained on p. 104, for the force whose components are  $F_R$  and  $F_{\phi}$  may be regarded as being made up in the following way: (1) a force  $\pi\rho\alpha^2\times$  (acceleration of the cylinder relative to the rotating axes); (2) a force  $\pi\rho\alpha^2\omega^2R$  acting towards the centre of rotation; and (3) a force  $2\pi\rho\alpha^2\omega\times$  (velocity of the cylinder relative to the rotating axes) acting at right angles to the direction of relative motion. These are evidently the same as the three forces discussed on p. 104.

Case 2.—The general motion of the fluid is one of uniform shearing. The fluid moves parallel to the axis of x with velocity  $\alpha y$ , which increases at a uniform rate as y increases. In this case  $\psi_1 = -\frac{1}{2} \alpha y^2$ , which may be written

$$\psi_1 = -\frac{1}{4}\alpha(x^2 + y^2) + \frac{1}{4}\alpha(x^2 - y^2).$$

Comparing this with (12) it appears that  $\zeta = -\frac{1}{2}\alpha$  and  $E' = \frac{1}{4}\alpha$ , while A' = C' = G' = 0. Hence from (7) and (14)

$$\psi = -\alpha \frac{r^2}{4} + \frac{\alpha^2 \dot{y}_0}{r} \cos \theta - \left\{ \alpha y_0 r + \frac{\alpha^2}{r} \left( \dot{x}_0 - \alpha y_0 \right) \right\} \sin \theta + \frac{\alpha}{4} \left( r^2 - \frac{\alpha^4}{r^2} \right) \cos 2\theta.$$

Hence differentiating and putting r = a,

$$\left[\frac{\partial^2 \psi}{\partial r \partial t}\right]_{r=a} = -\dot{y_0} \cos \theta + \dot{x_0} \sin \theta - 2\alpha \dot{y_0} \sin \theta,$$

$$\left[\frac{\partial \psi}{\partial r} + \dot{x}_0 \sin \theta - \dot{y}_0 \cos \theta\right]_{r=a} = \alpha (\cos 2\theta - \frac{1}{2}) - 2\dot{y}_0 \cos \theta + 2(\dot{x}_0 - \alpha y_0) \sin \theta,$$

$$\left[\frac{\partial}{\partial r}\left(\frac{\partial \psi}{r\partial \theta}\right)\right]_{r=a} = \frac{1}{a}\left\{2\dot{y}_0\sin\theta + (\dot{x}_0 - \alpha y_0)\cos\theta - 2\alpha\alpha\sin\theta\right\}.$$

Hence from (18)

$$-\frac{1}{\rho} \left[ \frac{\partial p}{\partial \theta} \right]_{r=a} = \ddot{x_0} \sin \theta - \dot{y_0} \cos \theta - 2 \alpha \dot{y_0} \sin \theta$$

$$+ \frac{2}{\alpha} \left\{ \dot{y_0} \sin \theta + (\dot{x_0} - \alpha y_0) \cos \theta - \alpha \alpha \sin 2\theta \right\}$$

$$\times \left\{ 2 \left( \dot{x_0} - \alpha y_0 \right) \sin \theta - 2 \dot{y_0} \cos \theta + \alpha \alpha \left( \cos 2\theta - \frac{1}{6} \right) \right\}.$$

Hence from (19)

$$\mathbf{F}_{z} = -\pi \rho \alpha^{2} \{ \dot{x}_{0} - \alpha \dot{y}_{0} \}, \qquad \mathbf{F}_{y} = -\pi \rho \alpha_{2} \{ \dot{y}_{0} + 2 \alpha (\dot{x}_{0} - \alpha \dot{y}_{0}) \}. \tag{20}$$

This result will now be applied to find the motion of a cylinder of the same density as the fluid when it is projected from the origin with velocity whose components are U and V.

The equations of motion of the cylinder are

$$\pi \rho a^2 \ddot{x_0} = -\pi \rho a^2 \{ \ddot{x_0} - 2 \alpha \dot{y_0} \}, \qquad \pi \rho a^2 \dot{y_0} = -\pi \rho \alpha^2 \{ \ddot{y_0} + 2 \alpha (\dot{x_0} - \alpha y_0) \},$$
or
$$\ddot{x_0} - \alpha \dot{y_0} = 0, \qquad \ddot{y_0} = -\alpha (\dot{x_0} - \alpha y_0).$$

The first of these may be integrated in the form

$$\dot{x}_0 - \alpha y_0 = \text{constant}.$$

That is to say, the component parallel to the axis of x of the relative velocity of the cylinder and the fluid is constant and equal to U. The acceleration of the cylinder in the direction of the axis of x is constant and equal to  $-\alpha V$ . If U=0, that is to say, if the cylinder is shot off in a direction perpendicular to the direction of shear, then the component of velocity parallel to the axis of y is constant, and the fluid pressure is just sufficient to give the cylinder the acceleration  $\alpha V$ , which is necessary in order that the velocity of the cylinder relative to the fluid round it may remain constant. This property of uniformly shearing fluids appears to be analogous to a certain extent to the property of rotating fluids discussed on p. 105.

# On Waves in an Elastic Plate. By Horace Lamb, F.R.S.

(Received July 10, 1916.)

The theory of waves in an infinitely long cylindrical rod was discussed by Pochhammer in 1876 in a well-known paper.\* The somewhat simpler problem of two-dimensional waves in a solid bounded by parallel planes was considered by Lord Rayleigh† and by the present writer‡ in 1889. The main object in these various investigations was to verify, or to ascertain small corrections to, the ordinary theory of the vibrations of thin rods or plates, and the wave-length was accordingly assumed in the end to be great in comparison with the thickness.

It occurred to me some time ago that a further examination of the two-dimensional problem was desirable for more than one reason. In the first place, the number of cases in which the various types of vibration of a solid, none of whose dimensions is regarded as small, have been studied is so restricted that any addition to it would have some degree of interest, if merely as a contribution to elastic theory. Again, modern seismology has suggested various questions relating to waves and vibrations in an elastic stratum imagined as resting on matter of a different elasticity and density. These questions naturally present great mathematical difficulties, and it seemed unpromising to attempt any further discussion of them unless the comparatively simple problem which forms the subject of this paper should be found to admit of a practical solution. In itself it has, of course, no bearing on the questions referred to.

Even in this case, however, the period-equation is at first sight rather intractable, and it is only recently that a method of dealing with it (now pretty obvious) has suggested itself. The result is to give, I think, a fairly complete view of the more important modes of vibration of an infinite plate, together with indications as to the character of the higher modes, which are of less interest. I may add that the numerical work has been greatly simplified by the help of the very full and convenient Tables of hyperbolic and circular functions issued by the Smithsonian Institution.

- \* 'Crelle,' vol. 81, p. 324; see also Love, 'Elasticity,' 1906, p. 275.
- t 'Proc. Lond. Math. Soc.,' vol. 20, p. 225; 'Scientific Papers,' vol. 3, p. 249.
- ‡ See 'Proc. Lond. Math. Soc.,' vol. 21, p. 85.
- § Love, 'Some Problems of Geodynamics,' 1911, Chap. XI.

<sup>&</sup>quot;'Hyperbolic Functions,' Washington, 1909. I have to thank Mr. J. E. Jones for kindly verifying and, where necessary, correcting my calculations.

1. The motion is supposed to take place in two dimensions x, y, the origin being taken in the medial plane, and the axis of y normal to this. thickness of the plate is denoted by 2f. The stress-strain equations are, in the usual notation,

$$p_{xx} = \lambda (\partial u/\partial x + \partial v/\partial y) + 2\mu \partial u/\partial x,$$

$$p_{xy} = \mu (\partial v/\partial x + \partial u/\partial y),$$

$$p_{yy} = \lambda (\partial u/\partial x + \partial v/\partial y) + 2\mu \partial v/\partial y.$$
(1)

It is known that the solution of the equations of motion is of the type

$$u = \partial \phi / \partial x + \partial \psi / \partial y, \qquad v = \partial \phi / \partial y - \partial \psi / \partial v, \qquad (2)$$

the functions  $\phi$ ,  $\psi$  being subject to the equations

$$\rho \frac{\partial^2 \phi}{\partial t^2} = (\lambda + 2\mu) \nabla^2 \phi, \qquad \rho \frac{\partial^2 \psi}{\partial t^2} = \mu \nabla^2 \psi, \tag{3}$$

where

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}.$$

We now assume a time-factor  $e^{i\sigma t}$  (omitted in the sequel), and write

$$h^2 = \frac{\rho \sigma^2}{\lambda + 2\mu}, \qquad k^2 = \frac{\rho \sigma^2}{\mu}, \tag{4}$$

so that

$$(\nabla^2 + h^2) \phi = 0, \qquad (\nabla^2 + h^2) \psi = 0. \tag{5}$$

We further assume, for the present purpose, periodicity with respect to x. This is most conveniently done by means of a factor  $e^{i\mathbf{t}\cdot\mathbf{r}}$ , the wave-length being accordingly

$$\lambda' = 2\pi/\xi. \tag{6}$$

Writing

$$\alpha^{2} = \xi^{2} - h^{2}, \qquad \beta^{2} = \xi^{2} - k^{2},$$
 (7)

we have

$$\frac{\partial^2 \phi}{\partial y^2} = \alpha^2 \phi, \qquad \frac{\partial^2 \psi}{\partial y^2} = \beta^2 \psi. \tag{8}$$

The equations (1) now give

$$\frac{\frac{\partial^{2}yy}{\mu} = (\xi^{2} + \beta^{2}) \phi - 2i\xi \frac{\partial \psi}{\partial y}, 
\frac{p_{xy}}{\mu} = 2i\xi \frac{\partial \phi}{\partial y} + (\xi^{2} + \beta^{2}) \psi.$$
(9)

Symmetrical Vibrations.

2. When the motion is symmetrical with respect to the plane y=0 we assume, in accordance with (8),

$$\phi = A \cosh \alpha y e^{i\xi x}, \qquad \psi = B \sinh \beta y e^{i\xi x}. \tag{10}$$

L

This gives, for the stresses on the faces  $y = \pm f$ ,

$$p_{yy}/\mu = \left\{ A \left( \xi^{2} + \beta^{2} \right) \cosh \alpha f - B \, 2 \, i \xi \beta \cosh \beta f \right\} e^{i \xi x},$$

$$p_{xy}/\mu = \pm \left\{ A \, 2 \, i \xi \alpha \sinh \alpha f + B \left( \xi^{2} + \beta^{2} \right) \sinh \beta f \right\} e^{i \xi x}$$

$$L - A$$
(11)

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Equating these to zero, and eliminating the ratio A/B, we have the period-equation\*

$$\frac{\tanh \beta f}{\tanh \alpha f} = \frac{4 \, \xi^3 \alpha \beta}{(\xi^2 + \beta^2)^3}. \tag{12}$$

In the most important type of long waves,  $\xi f$ ,  $\alpha f$ ,  $\beta f$ , are all small, and the limiting form of the equation is

$$(\xi^2 + \beta^2)^2 - 4\xi^2 \alpha^2 = 0, \tag{13}$$

whence

$$\frac{k^2}{\xi^2} = 4\left(1 - \frac{h^2}{k^2}\right) = \frac{4(\lambda + \mu)}{\lambda + 2\mu},\tag{14}$$

in virtue of (4). Hence if V be the wave-velocity

$$V^2 = \frac{\sigma^2}{\xi^2} = \frac{4(\lambda + \mu)\mu}{\lambda + 2\mu\rho}.$$
 (15)

This is in agreement with the ordinary theory, where the thickness is treated as infinitely small and the influence of lateral inertia is neglected.

For waves which are very *short*, on the other hand, as compared with the thickness 2f, the quantities  $\xi f$ ,  $\alpha f$ ,  $\beta f$  are large, and the equation tends to the form

$$(2\xi^2 - k^2)^2 - 4\xi^2 \alpha \beta = 0. \tag{16}$$

This is easily recognised as the equation to determine the period of "Rayleigh waves" on the surface of an elastic solid.† It is known that if the substance be incompressible  $(h = 0, \alpha = \xi)$  the wave-velocity is

$$V = 0.9554 (\mu/\rho)^{\frac{1}{2}}, \tag{17}$$

whilst on Poisson's hypothesis of  $\lambda = \mu$ ,

$$V = 0.9194 (\mu/\rho)^{\frac{1}{2}}.$$
 (18)

These results will, in fact, present themselves later.

3. In virtue of the relations (4), (7), the equation (12) may be regarded as an equation to find  $\sigma$  when  $\xi$  is given, *i.e.* to determine the periods of the various modes corresponding to any given wave-length; but from this point of view it is difficult to handle. It is easier to determine the values of  $\xi$  corresponding to given values of the ratio  $\beta/\alpha$ . This is equivalent to finding the wave-lengths corresponding to a given wave-velocity. Putting, in fact,  $\beta = m\alpha$ , we find from (7),

$$\xi^2 = \frac{k^2 - m^2 h^2}{1 - m^2},\tag{19}$$

and therefore

$$V^{2} = \frac{\sigma^{2}}{\xi^{2}} = \frac{k^{2}}{\xi^{2}} \frac{\mu}{\rho} = \frac{(\lambda + 2\mu)(1 - m^{2})}{\lambda + 2\mu - m^{2}\mu} \frac{\mu}{\rho}, \qquad (20)$$

so that V depends upon m only.

- \* An equivalent equation is given by Rayleigh.
- + Rayleigh, 'Proc. Lond. Math. Soc.,' vol. 17, p. 3 (1887); 'Scientific Papers,' vol. 2, p. 441.

4. For simplicity we will suppose in the first instance that the substance is incompressible, so that  $\lambda = \infty$ , h = 0,  $\alpha = \xi$ . Putting

$$\beta = m\xi, \qquad \xi f = \omega, \tag{21}$$

the equation (12) becomes

$$\frac{\tanh m\omega}{\tanh \omega} = \frac{4m}{(1+m^2)^2},\tag{22}$$

whilst

$$V^2 = (1 - m^2) \,\mu/\rho. \tag{23}$$

It is evident that real values of m must be less than unity. Moreover we have

$$\frac{d}{d\omega}\log\frac{\tanh m\omega}{\tanh \omega} = \frac{2}{\omega}\left(\frac{m\omega}{\sinh 2m\omega} - \frac{\omega}{\sinh 2\omega}\right),\tag{24}$$

which latter expression is easily seen to be positive so long as m < 1. Hence as  $\omega$  increases from 0, the first member of (22) increases from m to its asymptotic value unity. There is therefore one and only one value of  $\omega$  corresponding to any assigned value of m which makes the second member of (22) less than unity. And since

$$(1+m^2)^2 - 4m = (m-1)(m^3 + m^2 + 3m - 1), \tag{25}$$

the right-hand member of (22) is less than unity (for m < 1) only so long as m < 0.2956, which is the positive root of the second factor in (25). The admissible real values of m therefore range from 0.2956 to 0. The former of these makes  $\omega = \infty$ ,  $\lambda' = 0$ , and gives to V the value (17).

The values of  $\omega$  corresponding to a series of values of m between the above limits, together with the corresponding values  $(\lambda'/2f)$  of the ratio of wave-length to thickness, and the corresponding wave-velocities, are given in Table I (p. 118).

So far  $\beta$  has been taken to be real, or  $\xi < k$ . In the opposite case we may

write 
$$\beta_1^2 = k^2 - \xi^2, \qquad (26)$$

and assume 
$$\phi = A \cosh \alpha y e^{i\xi z}$$
,  $\psi = B \sin \beta_1 y e^{i\xi z}$ . (27)

The period-equation is then found to be

$$\frac{\tan \beta_1 f}{\tanh \alpha f} = \frac{4 \xi^2 \alpha \beta_1}{(\xi^2 - \beta_1^2)^2},\tag{28}$$

α being still supposed to be real.

In the case of incompressibility, writing

$$\xi f = \omega, \qquad \beta_1 = n\xi, \tag{29}$$

we have 
$$\frac{\tan n\omega}{\tanh \omega} = \frac{4n}{(1-n^2)^3},$$
 (30)

whilst 
$$V^2 = (1 + n^2) \mu / \rho.$$
 (31)

If as n increases from 0 we take always the lowest root of (30), we obtain a series of values of  $\omega$  continuous with the roots of (22) and diminishing down to zero, when  $n = \sqrt{3}$ . This latter value makes  $V = 2\sqrt{(\mu/\rho)}$ , in agreement with the general formula (15) for long waves. Numerical results for a series of values of n ranging from 0 to  $\sqrt{3}$  are included in Table I.

Table	I.—S	ymn	etric	al '	Type.	λ =	∞ .
	[The	unit	of V	is	$\sqrt{(\mu)}$	$\rho$ ).]	

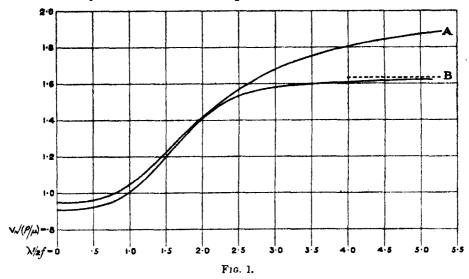
m.	n.	w.	λ'/2f.	V.
0 .2956		<b>o</b> o	0.0	0 -9554
0.29		8 67	0 .862	0.957
0.28		7 .09	0 442	0.960
0 .27		6 .38	0 .492	0 .968
0.26		5 .93	0:530	0.966
0.25		5 61	0.560	0.968
0.20		4.75	0.662	0.979
0.12		4 .35	0.722	0.889
0.10		4 14	0.759	0.995
0.02		4 .08	0.779	0.999
0.0	0.0	4.00	0.785	1.0
	0.1	3 .872	0 .811	1 .002
	0.2	3 570	0.880	1 .020
	0.3	3 .218	0.976	1 '044
	0.4	2 .883	1 .090	1 .077
	0.5	2 .587	1 .214	1 '118
	9.0	2 .331	1 .348	1 ·166
	0.7	2 108	1 .490	1.221
	0.8	1 .912	1 .643	1 .281
	0.8	1 .732	1 814	1 '845
-	1.0	Ìπ	2.0	√2
	1.1	1 417	2 · 217	1 487
	1 -2	1 ·269	2 476	1 .582
	1.3	1 ·121	2 803	1 640
	1.4	0 .967	8 .25	1 .721
	1 '5	0 ·798	8 .04	1 .808
	1.6	0.694	5 29	1 .887
	1 .7	0 ·292	10 .8	1 972
/	1.71	0 241	13.0	1 .981
	1 .72	0 ·175	18 .0	1 989
	1 .78	0 .081	88 88	1 1998
	√3	0.0	00	2.0

The relation between wave-length and wave-velocity for the whole series of modes investigated in this and in the preceding section is shown by the curve A on the opposite page. The unit of the horizontal scale is  $\chi'/2f$ ; that of the vertical scale is  $\chi'/2f$ .

5. On the present hypothesis of incompressibility there is a displacement function Ψ, analogous to the stream-function of hydrodynamics, viz., we have:—

$$u = \partial \Psi / \partial y, \qquad v = -\partial \Psi / \partial x.$$
 (32)

The lines  $\Psi = \text{const.}$  give the directions in which the particles oscillate, whilst if they are drawn for small equidistant values of the constant their



greater or less degree of closeness indicates the relative amplitudes. In the case of standing waves the system of lines retains its position in space; in the case of a progressive wave-train it must be imagined to advance with the waves.

If m be real we find, omitting a constant factor,

$$\Psi = \{2m \cosh m\omega \sinh \xi y - (1+m^2) \cosh \omega \sinh m\xi y\} e^{i\xi x}. \tag{33}$$

In the opposite case we may write

$$\Psi = \{2n\cos n\omega \sinh \xi y - (1 - n^2)\cosh \omega \sin n\xi y\}e^{i\xi x}. \tag{34}$$

I have thought it worth while to make diagrams illustrating the configuration of the lines of displacement in the class of modes of vibration which have so far been obtained.

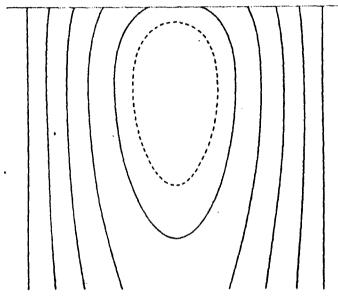
The case of the Rayleigh waves, corresponding to  $\omega = \infty$ , is, of course, of independent interest. In the present problem their wave-length is infinitely short; but if we transfer the origin to the surface y = f, and then make  $f = \infty$ , we get, omitting a numerical factor,

$$\Psi = (e^{m\xi y} - 0.5437 e^{\xi y}) e^{i\xi x}, \tag{35}$$

where m = 0.2956. On this scale the wave-length may have any value. The diagram (fig. 2) shows the great difference in the character of the motion, and the slow diminution of amplitude with increasing depth, as compared with the "surface waves" of hydrodynamics. It follows, in fact,

<sup>\*</sup> Lamb, 'Hydrodynamics,' 4th ed., art. 228.

from (35) that the ratio of the vertical amplitude to that at the surface (in the same vertical) at depths of  $\frac{1}{4}$ ,  $\frac{1}{2}$ , 1 wave-length, is 1.30, 0.814, 0.340, respectively, whereas in the hydrodynamical problem the corresponding numbers are 0.208, 0.043, 0.002.



F1G. 2.

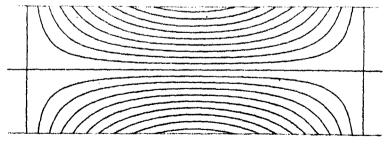
In the case of  $\xi < k$ , the displacement function is given by (34). I have chosen for illustration, as giving a wave-length neither too great nor too small, the case of n = 1.6, which makes

$$\omega = 0.594$$
,  $n\omega = 0.950$ ,  $\lambda'/2f = 5.29$ ,

and, accordingly,

$$\Psi = (1.010 \sinh \xi y + \sin n\xi y) e^{i\xi x}. \tag{36}$$

The result is shown in fig. 3, which, like the former diagram, covers half a wave-length. The diagram may be taken to illustrate also, in a general



F1G. 3.

way, the most important type of longitudinal vibrations in a cylindrical rod.

6. The modes of vibration so far obtained include all the more interesting types, from the physical point of view, of the symmetrical class; but there are, of course, an infinity of others. These correspond to the higher roots of the equation (30). Thus when n = 0.1 we easily find the approximate solutions

$$\omega/\frac{1}{2}\pi = 22.47, \quad 42.47, \quad 62.47, \dots$$
 (37)

For n = 0.2

$$\omega/\frac{1}{2}\pi = 12.28, \quad 22.28, \quad 32.48, \dots$$
 (38)

For n = 0.3

$$\omega/\frac{1}{2}\pi = 8.72, 15.39, 22.05, \dots;$$
 (39)

and so on.

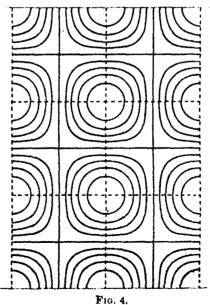
In these modes the plane xy is mapped out into rectangular compartments whose boundaries are lines of displacement. This may be illustrated by the case of n=1, when the internal compartments are squares. This happens to be particularly simple mathematically. The formula (34) for  $\Psi$  is now indeterminate, but is easily evaluated. It is found from (30) that for small concomitant variations of  $\omega$  and n about n=1 we have  $\delta(\omega n)=0$ . This leads to

$$\Psi = \sin \xi y \, e^{i\xi x},\tag{40}$$

with

$$\xi = (2s+1)\pi/2f, (41)$$

where s is an integer. The configuration is shown in fig. 4 for the case



s=1; but it is to be observed that the dotted lines in the diagram all represent planes which are free from stress, and that consequently any combination of them may be taken to represent free boundaries. This particular solution is, moreover, independent of the hypothesis of incompressibility.\* The surface-conditions (11) are, in fact, satisfied by

$$A = 0, \quad \xi^2 - \beta_1^2 = 0, \quad \cos \beta_1 f = 0,$$
 (42)

which lead again to (40) and (41).

As n is increased the compartments referred to become more elongated. For large values of n, and consequently small values of  $\omega$  or  $\xi f$ , we have in the limit  $n\omega = s\pi$ , where s is integral. It is otherwise evident that the surface conditions are satisfied by

$$\mathbf{A} = 0; \quad \boldsymbol{\xi} = 0, \quad \sin \beta_1 f = 0, \tag{43}$$

whence

$$\phi = 0, \qquad \psi = B \sin(s\pi y/f). \tag{44}$$

The vibration now consists of a shearing motion parallel to x, with 2s nodal planes symmetrically situated on opposite sides of y = 0. The frequency is given by

$$\sigma^2 = \frac{8^2 \pi^2}{f^2} \frac{\mu}{\rho}.\tag{45}$$

#### Asymmetrical Modes.

7. When the motion is anti-symmetrical with respect to the plane y=0 we assume

$$\phi = A \sinh \alpha y e^{i\xi x}, \qquad \psi = B \cosh \beta y e^{i\xi x},$$
 (46)

where  $\alpha$ ,  $\beta$  are defined as before by (7). This gives for the stresses at the planes  $y = \pm f$ ,

$$p_{yy}/\mu = \pm \left\{ A(\xi^{2} + \beta^{2}) \sinh \alpha f - B 2i\xi\beta \sinh \beta f \right\} e^{i\xi x},$$

$$p_{xy}/\mu = \left\{ A 2i\xi\alpha \cosh \alpha f + B(\xi^{2} + \beta^{2}) \cosh \beta f \right\} e^{i\xi x}.$$
(47)

These surfaces being free, we deduce

$$\frac{\tanh \beta f}{\tanh \alpha f} = \frac{(\xi^2 + \beta^2)^2}{4 \xi^2 \alpha \beta}.$$
 (48)

\* It was noticed long ago by Lamé as a possible mode of transverse vibration (uniform throughout the length) in a bar of square section, 'Théorie mathématique de l'élasticité,' 2nd ed., p. 170.

There is an analogous solution in the case of the symmetrical vibrations of a cylindrical rod. The surface-conditions given on p. 277 of Love's 'Elasticity' (equation (54)) are satisfied by

$$A = 0$$
,  $J_1'(\kappa'\alpha) = 0$ ,  $2\gamma^2 = p^2\rho/\mu$ .

In the notation of this paper the latter two conditions would be written

$$J_1'(\beta,a) = 0, \quad 2\xi^2 = k^2$$

† Cf. Rayleigh, loc. cit.

When the waves are infinitely short this reduces to the form (16) appropriate to Rayleigh waves.

In the case of long flexural waves  $\alpha f$ ,  $\beta f$ ,  $\xi f$  are small. Writing

$$\tanh \alpha f = \alpha f (1 - \frac{1}{3} \alpha^2 f^2), \qquad \tanh \beta f = \beta f (1 - \frac{1}{3} \beta^2 f^2),$$

$$h^2 = 4 (1 - h^2 / k^2) \xi^2 f^2. \tag{49}$$

on the supposition that  $k^2/\xi^2$ ,  $k^2/\xi^2$  are small, which is seen to be verified. This makes

$$V^{2} = \frac{4}{3} \xi^{2} f^{2} \frac{\lambda + \mu}{\lambda + 2\mu} \frac{\mu}{\rho}, \tag{50}$$

in agreement with the ordinary approximate theory.

we find

It may be pointed out in this connection that Fourier's well-known calculation\* of the effect of an arbitrary initial disturbance in an infinitely long bar is physically defective, in that it rests on the assumption that the formula analogous to (50) is valid for all wave-lengths. As a result, it makes the effect of a localised disturbance begin instantaneously at all distances, whereas there is a physical limit, viz.  $\sqrt{\{(\lambda+2\mu)/\rho\}}$ , to the rate of propagation.

8. For the purpose of a further examination we assume the substance of the plate to be incompressible, so that  $\alpha = \xi$ , and write  $\beta = m\xi$  as before. The equation (48) becomes

$$\frac{\tanh m\omega}{\tanh \omega} = \frac{(1+m^2)^2}{4m},\tag{51}$$

where  $\omega = \xi f$ . The wave-velocity is given by (23).

Since m must be less than unity, whilst the second member of (51) exceeds 1 if m < 0.2956, it appears that for real solutions we are restricted to values of m between 0.2956 and 1. A series of values of  $\omega$  corresponding to values of m within this range is given on the next page.

The displacement-function is found to be

$$\Psi = \{(1+m^2)\cosh m\omega \cosh \xi y - 2\cosh \omega \cosh m\xi y\} e^{i\xi z}. \tag{52}$$

The forms of the lines  $\Psi = \text{const.}$  for the case of

$$m = 0.9$$
,  $\omega = 0.435$ ,  $m\omega = 0.392$ ,  $\lambda'/2f = 7.22$ ,

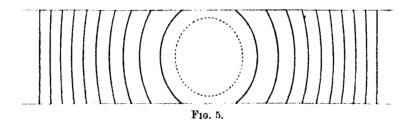
are shown in fig. 5, for a range of half a wave-length. Regarded as belonging to a standing vibration, they indicate a rotation of the matter in the neighbourhood of the nodes, about these points.

<sup>\*</sup> See Todhunter, 'History of the Theory of Elasticity,' vol. 1, p. 112; Rayleigh, Theory of Sound,' vol. 1, art. 192.

191.	w.	λ'/2f.	v.
0 .2956	<b>6</b> 0	0.0	0.9554
0.80	8 84	0.856	0 954
0 .82	4 .30	0.748	0 .987
0.40	3 .028	1 .088	0.917
0.45	2 ·879	1 821	0.893
0.50	1 946	1 '614	0.866
0.55	1 .627	1 .981	0.835
0.60	1 .877	2 .282	0.800
0.85	1 .171	2 .683	0.760
0.70	0 .995	8 157	0.714
0.75	0 .841	3 ·736	0.661
0.80	0 .700	4 ·45	0.600
0.85	0.268	5 ·58	0.527
0.80	0.485	7 ·22	0 .436
0 .95	0.800	10 · 5	0 .812
1.0	0.0	∞	0.0*

Table II.—Asymmetrical Type.  $\lambda = \infty$ . [The unit of V is  $\sqrt{(\mu/\rho)}$ .]

<sup>\*</sup> For small values of \$f the value of V is given by equation (50).



So far it has been supposed that  $k < \xi$ , and consequently that m is real. In the opposite case we assume in place of (46)

$$\phi = A \sinh \alpha y e^{i\xi x}, \qquad \psi = B \cos \beta_1 y e^{i\xi x},$$
 (53)

and the period-equation is

$$\frac{\tan \beta_1 f}{\tanh \alpha f} = -\frac{(\xi^2 - \beta_1^2)^2}{4 \xi^3 \alpha \beta_1},$$
 (54)

where  $\beta_1$  is defined by (26).

In the case of incompressibility this becomes

$$\frac{\tan n\omega}{\tanh \omega} = -\frac{(1-n^2)^2}{4n},\tag{55}$$

where  $\omega = \xi f$ ,  $n = \beta_1/\xi$ . As the preceding investigation (summarised in Table II) evidently covers all the modes in which v has the same sign throughout the thickness, the additional modes to which this equation relates may be dismissed with the remark that they are analogous to those referred

to in § 6 above. The particular case n = 1 is illustrated by fig. 4 if we imagine the lowest horizontal dotted line to form the lower boundary.

# Influence of Compressibility.

9. Although the hypothesis of incompressibility has been adopted for simplicity, the numerical calculations, so far as the more important modes are concerned, are not much more complicated if we abandon this restriction. It will be sufficient to consider the case of the symmetrical types.

We have from (4) and (7)

$$\xi^{2} = \frac{k^{2}\alpha^{2} - h^{2}\beta^{2}}{k^{2} - h^{2}} = \frac{(\lambda + 2\mu)\alpha^{2} - \mu\beta^{2}}{\lambda + \mu}.$$
 (56)

Hence if we write

$$\alpha f = \omega, \qquad \beta = m\alpha, \tag{57}$$

the equation (12) takes the form

$$\frac{\tanh m\omega}{\tanh \omega} = 4m \frac{(\lambda + \mu)(\lambda + 2\mu - m^2\mu)}{(\lambda + 2\mu + m^2\lambda)^3}.$$
 (58)

The relation of  $\omega$  to the wave-length is given by

$$\xi^2 f^2 = \frac{(\lambda + 2\mu - m^2\mu)\,\omega^2}{\lambda + \mu},\tag{59}$$

whilst the wave-velocity is given by (20).

For numerical illustration, we may adopt Poisson's hypothesis as to the relation between the elastic constants. Putting, then,  $\lambda = \mu$ , we have

$$\frac{\tanh m\omega}{\tanh \omega} = \frac{8m(3-m^2)}{(3+m^2)^2},\tag{60}$$

$$\xi f = \sqrt{(\frac{1}{2}(3-m^2))}\omega, \qquad V^2 = \frac{3(1-m^2)}{3-m^2}\frac{\mu}{\rho}.$$
 (61)

Real values of m must lie between 0 and 0.4641, this being the positive root of the equation

$$m^3 + 9m^2 + 15m - 9 = 0 (62)$$

obtained by equating the second member of (60) to unity. The wave-velocity corresponding to this latter value of m is

$$V = 0.9194 \sqrt{(\mu/\rho)}, \tag{63}$$

in accordance with the theory of Rayleigh waves, the wave-length being now infinitely small compared with the thickness.

When m is imaginary (=in), we have

$$\frac{\tan n\omega}{\tanh \omega} = \frac{8n(3+n^2)}{(3-n^2)^2},$$
 (64)

$$\xi f = \sqrt{\left[\frac{1}{2}(3+n^2)\right]}\omega, \qquad V^2 = \frac{3(1+n^2)}{3+n^2}\frac{\mu}{\rho}.$$
 (65)

The more important modes coming under these formulæ are determined by the lowest root of (64) for values of n ranging from 0 to  $\sqrt{15}$ , this latter number corresponding to an infinitesimal value of  $\omega$ , *i.e.* to waves of infinite length.

Numerical results are given in Table III, and the relation between wave-length and wave-velocity is shown by the curve B in fig. 1 (p. 119). The unit of the vertical scale is  $V/\sqrt{(\mu\rho^{-1})}$  as before.

Table III.—Symmetrical Type.  $\lambda = \mu$ . [The unit of V is  $\sqrt{(\mu/\rho)}$ .]

m.	n.	ω,	λ'/2f.	v.
0 4641		•	0.0	0 .9194
0 45	AMERICA	5 ·220	0 .509	0.925
0 '40		8 .807	0 .692	0.942
0.85	_	3 · 848	0.784	0.956
0.80		3 '085	0.844	0.969
0 .25		2 .918	0 .888	0.978
0.20		2 .805	0 .921	0.986
0.15		2 .727	0.944	0.992
0.10		2 .678	0 .959	0 .997
0.0	0.0	2 .640	0.972	1.0
-	0.1	2 .604	0.888	1 .003
_	0.2	2.506	1.017	1 .013
	0.4	2 214	1 ·129	1.049
	0.6	1 .911	1 .268	1 102
F. W. W.	0.8	1 649	1 412	1 .163
m ##	1.0	1 · 482	1 .221	1 .225
***	1 .2	1 .253	1 .688	1 .284
	1.4	1:105	1 .802	1 .888
	1 .6	0.979	1 .024	1 .386
	√3	0.907	2.0	√2
	1.8	0.872	2 04	1 428
	2.0	0.778	2.16	1 .464
	2 ·2	0.696	2 ·28	1 495
h-han	2 ·4	0.620	2 .42	1 .522
	2.6	0 .551	2 .58	1 .544
	2.8	0 .486	2 .78	1 .264
	8.0	0 .422	8 04	1.581
	3 ·2	0.859	8 .40	1 .296
The same	8.4	0 .292	8 -99	1 .609
r was sales.	8.6	0.216	5 .15	1.620
	8.8	0 109	9.8	1 680
	√15	0.0	<b>x</b> 0	1 '688

As n increases from 0, the modes corresponding to the higher roots of (64) have at first the same general character as in the case of incompressibility

(§ 6). When  $n = \sqrt{3}$ , we have the division into square compartments, to which fig. 4 refers. When n is infinite, whilst  $n\omega$  is finite, we have

$$\alpha = 0, \quad \beta_1 f = n\omega = s\pi, \quad \xi f = s\pi/\sqrt{2}.$$
 (66)

A reference to (11) shows, in fact, that, independently of any special relation between the elastic constants, the boundary conditions are satisfied by  $\alpha = 0$ ,  $\sin \beta_1 f = 0$ ,

and 
$$A(\xi^2 - \beta_1^2) + 2B\xi\beta_1 \cos s\pi = 0.$$
 (67)

This leads to

$$u = i \left( \cos s\pi + \frac{\lambda}{2\mu} \cos \frac{s\pi y}{f} \right) e^{i\xi x},$$

$$v = \sqrt{\left\{ \frac{\lambda^2}{\mu(\lambda + \mu)} \right\} \sin \frac{s\pi y}{f} e^{i\xi x}}.$$
(68)

There is here a transition to the case where  $\alpha$ , as well as  $\beta$ , is imaginary. Writing

$$\alpha_1^2 = h^2 - \xi^2, \qquad \beta_1^2 = k^2 - \xi^2, \tag{69}$$

and assuming (for the case of symmetry)

$$\phi = A \cos \alpha_1 y \, e^{i\xi x}, \qquad \psi = B \sin \beta_1 y \, e^{i\xi x}, \tag{70}$$

the period-equation is found to be

$$\frac{\tan \beta_1 f}{\tan \alpha_1 f} = -\frac{4 \xi^2 \alpha_1 \beta_1}{(\beta_1^2 - \xi^2)^2}.$$
 (71)

Since

$$\xi^{2} = \frac{h^{2}\beta_{1}^{2} - k^{2}\alpha_{1}^{2}}{k^{2} - h^{2}} = \frac{\mu \beta_{1}^{2} - (\lambda + 2\mu) \alpha_{1}^{2}}{\lambda + \mu},$$
 (72)

we find, writing

$$\alpha_1 f = \omega, \qquad \beta_1 f = q \omega, \tag{73}$$

$$\frac{\tan q\omega}{\tan \omega} = 4(\lambda + \mu) \frac{q(\lambda + 2\mu - q^2\mu)}{(q^2\lambda + \lambda + 2\mu)^2}.$$
 (74)

Also

$$\xi^{2} f^{2} = \frac{q^{2} \mu - (\lambda + 2\mu)}{(\lambda + \mu)} \omega^{2},$$

$$V^{2} = \frac{(\lambda + 2\mu)(q^{2} - 1)}{q^{2} \mu - (\lambda + 2\mu)} \frac{\mu}{\rho}.$$
(75)

On Poisson's hypothesis these become

$$\frac{\tan q\omega}{\tan \omega} = \frac{-8q (q^2 - 3)}{(q^2 + 3)^2},\tag{76}$$

$$\xi f = \sqrt{\left[\frac{1}{2}(q^2 - 3)\right]} \omega, \qquad V^2 = 3 \frac{q^2 - 1}{q^2 - 3} \frac{\mu}{\rho}. \tag{77}$$

The value of q may range downwards from  $\infty$  to  $\sqrt{3}$ .

A minute examination of these modes would be laborious, and would hardly repay the trouble. In the extreme case where  $q = \sqrt{3}$ , the equation (76) is satisfied by either a zero value of  $\tan q\omega$ , or an infinite value of  $\tan \omega$ . The former alternative gives the shearing motions parallel to x, already referred to at the end of § 6 (equations (43) and (44)). The other alternative gives a vibration at right angles to x. It is, in fact, obvious from (11) that the conditions are satisfied by

$$\xi = 0$$
,  $B = 0$ ,  $\cos \alpha_1 f = 0$ , (78)

whence

$$\phi = \cos(2s+1)\frac{\pi y}{2f}, \qquad \psi = 0, \tag{79}$$

$$\sigma^2 = (s + \frac{1}{2})^2 \frac{\pi^2}{f^2} \frac{\lambda + 2\mu}{\rho}.$$
 (80)

When q slightly exceeds  $\sqrt{3}$ , we have modes of vibration resembling the above types, except for a gradual change of phase in the direction of x. The corresponding values of V, as given by (77), are very great, but it is to be remarked that the notion of "wave-velocity" is in reality hardly applicable (except in a purely geometrical or kinematical sense) to cases of this kind, and that results relating to modes lying outside the limits of the numerical Tables are more appropriately expressed in terms of frequency.\* As already remarked, there is a physical limit to the speed of propagation of an initially local disturbance.

<sup>\* (&#</sup>x27;f. 'Hydrodynamics,' art. 261, where a similar point arises.

Magnetic Induction and its Reversal in Spherical Iron Shells.\*

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(Communicated by Prof. J. A. Fleming, F.R.S. Received November 30, 1916.)

In a previous communication to the Society, an account was given of an investigation of the magnetic shielding of a large space, by the use of a series of spherical iron shells. The basis of this investigation, which is still in progress, is strictly quantitative, and the work has been retarded, to a great extent, by the fact that several processes adopted commonly by various investigators of magnetic phenomena have never been examined accurately on the theoretical side, and in several cases even on the experimental side, to an order of precision which is sufficient for delicate measurements. One of the main objects ultimately in view, in the work described already, is the production, throughout the volume of a large iron specimen, of a magnetic field so small, in comparison with that of the earth, for example, as to render possible some accurate conclusions regarding the behaviour of iron under indefinitely small magnetic forces. This behaviour is at present a matter of doubt, and it remains to be shown that the indications of its real nature, obtained in earlier papers by one of us, continue to point in the same direction when the force is decreased below any values which have been In the experiments described in the former paper, a employed hitherto. field so low as 0.0033 C.G.S. unit was obtained in a spherical space of radius 32.5 cm. by the use of four concentric shells. It was accompanied, however, by a leakage field of 0.006 C.G.S. unit, and the shells still showed some traces of permanent polarisation after continued treatment with many reversals of a slowly decreasing current.

This method of demagnetisation is used extensively, and in its application coils have sometimes been wound somewhat loosely on the iron to be demagnetised, and the constant field given by Maxwell's formula for a spherical internal space surrounded by a very closely wound coil assumed to exist. But if a thin shell is wound in this manner, although the more internal parts may be subject to this field, the results must be widely different in the outer material of the shell. Further experimental work on

<sup>\*</sup> We wish again to acknowledge a grant for the purpose of researches on shielding, which was voted to us by the Council of the Society out of the Gore Fund.

<sup>† &#</sup>x27;Roy. Soc. Proc.,' A, vol. 92, p. 529 (1916).

the improvement of magnetic shielding beyond the order obtained alreadyin fact by such methods as the employment of a very small magnetising current to remove, in the internal space, the small part of the earth's field which may remain after the operation of the shielding effect of a set of shells -requires a precise knowledge of the value of the magnetic induction in a shell, or one member of a set of shells, wound by a spherical helical coil. For the condition of indefinitely close packing is found to be essential to the success of Maxwell's formula, which—but only from this particular point of view—does not appear, either from an a priori theoretical consideration, or from the experimental results described in the present paper, to have the large range of validity which has been assumed for it hitherto by practical workers on magnetic phenomena.

It is noteworthy that Maxwell himself did not claim any validity for his expression of the force inside a spherical helix when that helix was not in fact in the ideal state of indefinitely close winding. The use of such a helix for the purpose of demagnetisation of a hollow shell-where importance attaches more to the material of the shell than to the air space within—was not adopted at that time, and the practical problem had given no indication of its ultimate importance. Evidently the spacing of the helix constituting an ordinary cylindrically wound solenoid, if small in comparison with the radius of the cylinder, would not seriously disturb the uniform distribution of magnetic induction in a thin iron bar placed along its axis, but at the outer surface of a thick bar filling the helix the distribution would be widely different. We may argue from this by analogy to the spherically wound thin iron shells whose thickness is of the same order as the space between consecutive turns of the coil.

Apart from the case of a closely wound coil on a shell of non-magnetisable material, Maxwell did not consider the problem of the spherical helix in further detail. No subsequent writer has taken up the question, and it has been necessary to include in this paper some preliminary theoretical discussion of the problems whose experimental investigation has been required. calculations relate to the ideal case of indefinitely close winding-no simple mathematical treatment of a more practical case has yet been found—and the results are compared with those found for the actual coils which were described in the earlier paper. An estimate of the effect of spacing in the helix is thus obtained, and the calculations are of importance in themselves. as indicating some quantitative relations, inherent in problems of this nature. which it would be difficult to obtain by general reasoning. The distribution of magnetic induction in a set of shells, all of which may possess magnetising helices internally and externally, follows certain very curious laws.

Into the experimental problem of reversal of the magnetic induction of a shell, two main factors enter. The first is the nature of the magnetising coil and the necessary current it must contain. As stated already, the investigation of this problem is one of the main objects of the present paper. But in addition, demagnetisation of a mass of iron is much retarded by eddy currents set up in the iron by any change applied to the magnetising forces. These currents, while flowing, shield the inner shells, in the case of a set, from the effect of the changed field, and if the reversals of current in the coils are made too quickly, the process is very inefficient as a demagnetising agency, for, in the time occupied by two reversals, the effect does not penetrate to the inner part of the iron.

The latter part of the paper contains a further contribution to the study of this phenomenon, as it is necessary to obtain some estimate of the time required between reversals, for small values of the magnetic induction. Previous work on eddy current phenomena has been almost completely restricted to cases in which the average magnetic induction is of a much higher order of magnitude than in the present experiments.

Before proceeding to a description of the experimental work, it is desirable to give some account of the solution of the theoretical problems which are involved, and which have not hitherto received attention. required throughout, however, is a fairly simple extension of a well-known method of treating a set of shells without magnetising coils, and for this reason the work is set out somewhat briefly, and, in certain of the cases, only the final results are quoted when there is no novelty in the mode of treatment or when the complete investigation is somewhat long, and only interesting from the point of view of its final results. No attempt is made to deal with other than the ideal cases in which the magnetising helices are wound extremely closely. In this manner, two simple surface conditions become applicable at every coil—the continuity of normal magnetic force, and a discontinuity of a prescribed amount in the magnetic potential—as shown in the following section. But the distribution of magnetic induction in the actual set of shells must be similar, in a general manner, to that calculated for these ideal cases, whose consideration has, in fact, served to direct the experimental work into the most fruitful channels.

## The Spherically Wound Magnetising Coil.

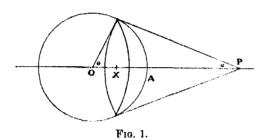
The fact that a coil wound closely over a sphere of unit permeability, with all its turns perpendicular to the same diameter, produces a uniform internal field is well known.\* For a diameter 2a, with 2na turns each carrying a current i,

\* Maxwell's 'Electricity and Magnetism,' vol. 2, para. 675 (ed. 1873).

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the strength of the field is \*\*\pirin\* parallel to the diameter. Maxwell quotes also the formula for the magnetic potential outside such a region in the same circumstances, as the result of a very general investigation into the theory of current sheets. It can, however, be obtained at once by direct integration and, as the need for such a proof appears to be marked, the investigation follows.

If OA is the diameter, and there are n turns per unit length of diameter, the number in any section of centre X is ndx, each carrying a current i,



where x = OX. The solid angle subtended at P by these currents is  $2\pi (1-\cos \alpha)$ , where  $\alpha$  is the angle in the figure, and, for a radius  $\alpha$  of the sphere, the magnetic potential of the whole system at P is

$$\Omega = \int_{-a}^{a} 2\pi i n \left(1 - \cos \alpha\right) dx,$$

where, if OP = z,

$$x = a\cos\theta = a\mu$$
,  $(a^2 + z^2 - 2az\cos\theta)^{\frac{1}{2}}\cos\alpha = z - a\cos\theta$ ,

and thus

$$\Omega = 2 \pi i n a \int_{-1}^{1} \left\{ 1 - \frac{z - a \mu}{(z^2 + a^2 - 2 a z \mu)^{\frac{1}{6}}} \right\} d\mu.$$

The integral may be evaluated readily to

$$\Omega = 4 \pi i n a^3/z^3$$

which may be generalised at once after the usual manner of potential theory to

$$\Omega = 4\pi i n a^3/r^3 \cdot \cos \theta$$
.

at an external point  $(r, \theta)$  referred to the centre and diameter. The external effect is therefore that of a simple magnetic doublet of moment  $4\pi i n a^3$ , situated at the centre of the sphere.

The normal magnetic intensity on the surface of the sphere is  $-\partial\Omega/\partial r$  with r=a, or  $\frac{a}{\pi}$  rina  $\cos\theta$ , and is continuous with that derived from the

internal potential  $\Omega = -\frac{8}{8}\pi inr\cos\theta$ . The potential itself, on the other hand, is discontinuous at r = a, for

$$\Omega_{\rm out} - \Omega_{\rm in} = a \left( \frac{4}{3} \pi i n + \frac{8}{3} \pi i n \right) \cos \theta = 4 \pi i n a \cos \theta,$$

so that the amount of the discontinuity is  $4\pi ina\cos\theta$ . These constitute the two surface conditions mentioned already as applicable at the surface of the coil, and they admit of an instructive comparison with the corresponding conditions for a spherical shell magnetised normally at every point—the discontinuity of potential is in this case  $4\pi\phi$ , where  $\phi$  is the strength of the shell.

We may now consider a spherical helix wound closely on a shell of non-magnetic material, enclosing a concentric shell, of inner and outer radii a and b, and of permeability  $\mu$ . The radius of the coil is c, and it is wound with n turns per unit length of diameter, each carrying a current i. With the origin at the centre, and the diameter perpendicular to the windings as initial line of polar co-ordinates, the field in the hollow of the inner shell may be defined by a potential  $\Omega_1 = Ar \cos \theta$ , whereas in the magnetic material of the inner shell the potential is of the form

$$\Omega_2 = (Br + C/r^2)\cos\theta.$$

Capital letters denote constants as usual. Between this shell and the coil, and outside the coil, the potentials are respectively

$$\Omega_3 = (\mathrm{D}r + \mathrm{E}/r^2)\cos\theta, \qquad \Omega_4 = \mathrm{F}/r^2 \cdot \cos\theta.$$

The usual conditions are fulfilled at the two surfaces of the shell of permeability  $\mu$ , thus

A = B+C/
$$a^3$$
 =  $\mu$  (B-2C/ $a^3$ ), B+C/ $b^3$  = D+E/ $b^3$ ,  
 $\mu$  (B-2C/ $b^3$ ) = D-2E/ $b^3$ .

These four equations may be supplemented by the conditions at the coil, where r = c. These are

$$\partial \Omega_8/\partial r = \partial \Omega_4/\partial r$$
 and  $\Omega_4 - \Omega_3 = 4\pi inc \cos \theta$ .

Accordingly

$$D-2E/c^8 = -2F/c^3$$
,  $D+E/c^3 = -4\pi in + F/c^3$ ,

whence

$$D = -\frac{8}{5}\pi in, \qquad C = -\frac{8\pi ina^3(\mu - 1)}{9\mu + 2(\mu - 1)^3(1 - a^3/b^3)},$$

$$B = -\frac{8\pi in(2\mu + 1)}{9\mu + 2(\mu - 1)^2(1 - a^3/b^3)},$$

from the solution of the six equations. These values are, as might be expected, independent of the radius of the magnetising coil, which remains

equivalent, in its effect on an inside iron shell, to a uniform magnetic field external to the shell.

The most convenient magnitude for measurement in such a thin shell is the maximum transverse induction (transverse to the radius vector at  $\theta = 90^{\circ}$ ) when the use of an exploring coil is adopted, as in succeeding experiments. Now, the magnetic potential in the material is

$$\Omega_2 = (Br + C/r^2)\cos\theta,$$

and the transverse magnetic induction is  $-\mu\partial\Omega_2/r\partial\theta$  or  $-\mu$  (B+Cr<sup>-3</sup>) sin  $\theta$ . It is greatest in the plane  $\theta = 90^{\circ}$ , and the average value in that plane, denoted subsequently by B<sub>max.</sub>, is

$$B_{\text{max.}} = -\frac{2\mu}{b^2 - a^2} \int_a^b (B + Cr^{-3}) r dr = \mu B + \frac{2\mu C}{ab(a+b)}.$$

For a thin shell, the variation across the section  $\theta = 90^{\circ}$ , or any other section, is so small that  $\mu(B+Ca^{-3})$  may be used for  $B_{max}$ , so that, quoting the values of B and C, we obtain

$$B_{\text{max.}} = -\frac{24\pi i n \mu^2}{9\mu + 2(\mu - 1)^2 (1 - a^3/b^3)}.$$

If  $1-a^3/b^3=3\epsilon$ , where, in the subsequent experiments,  $\epsilon$  is about  $\frac{1}{15}$ ,

$$B_{\text{max.}} = -8\pi i n \mu/(3 + 2\mu\epsilon)$$

to a good approximation.

It is, perhaps, desirable at this point to lay some emphasis on the smallness of the values of B<sub>max</sub>, produced in a single shell by the demagnetising currents adopted in the experiments described in the former paper.  $\epsilon = \frac{1}{15}$ ,  $n = \frac{1}{2}$ , and  $\mu = 150$ , a current of 1 ampère, or  $10^{-1}$  C.G.S. unit which was the order of the magnitude of the current used—only produces an average magnetic induction, in a single shell, of amount

$$_{3}^{4}_{6}\pi \times 150/23 = 8.5$$
 C.G.S. units,

at  $\theta = \pi/2$ . The actual value will be even smaller, on account of the loose winding of the coil, which corresponds to  $n=\frac{1}{2}$ .

Consider now a magnetising coil, of radius e, wound internally to the shell of radii a and b, perhaps on a shell of non-magnetic material in the interior. The fields in the various regions are represented very simply. In the space internal to the coil the field is uniform, whereas between the coil and shell. and in the material of the shell, it can in each case be represented by the superposition of a uniform field and that of a central magnetic doublet of suitable moment. Outside the shell, being finite at infinity, it is the field of a central magnetic doublet only. There is no necessity to record the

analysis, which follows the same lines as before. The final magnetic potential in the material of the shell is found to be

$$\Omega = (Ar + B/r^2)\cos\theta,$$

where

$$\mathbf{A} = \frac{8\pi i n (\mu - 1) c^3 / b^3}{9\mu + 2 (\mu - 1)^2 (1 - a^3 / b^3)}, \qquad \mathbf{B} = \frac{4\pi i n c^3 (\mu + 2)}{9\mu + 2 (\mu - 1)^2 (1 - a^3 / b^3)}.$$

The average value of B<sub>max.</sub>, obtained as before, is

$$B_{\text{max.}} = \mu A + 2 \mu B / ab (a+b),$$

or, to a close approximation for a thin shell,

$$B_{\text{max.}} = \frac{12\pi i n \mu^2 c^3 / b^3}{9\mu + 2(\mu - 1)^2 (1 - a^3 / b^3)}$$

directly proportional to the cube of the radius of the coil. If the coil is effectively wound on the inner surface of the thin shell of magnetic material, we may put c=a, and comparison with the previous case indicates an interesting theorem:—

The maximum transverse magnetic inductions obtained by winding a thin iron shell (1) internally, and (2) externally, with the same coil carrying the same current are in the ratio 1:2.

No conclusion, however, can be drawn from this result as regards the relative maxima induced simultaneously in two thin shells of nearly equal radii with a coil wound in the small air space between them. Their mutual effect is then of great importance and is considered in the next section.

### Two Concentric Shells enclosing a Magnetising Coil.

The analysis of the arrangement is somewhat long, but it follows the previous lines so closely that we only present a bare summary. Let (a, b)and (d, e) be the two radii of the inner and outer shells, each of permeability  $\mu$ , and let c be the radius of the coil situated between them, so that a, b, c, d, e are in ascending order of magnitude. Between r = a and b, b and c, c and d, and d and e, two constants are in each case required to define the magnetic potential when a current is passed through the coil. When r = athe field is uniform, and beyond r = e it is that of a central magnetic doublet. Each of these two regions requires one constant, so that, for a complete specification of the magnetic distribution produced by the current, 10 constants must be determined: The usual conditions at the four surfaces of the shells lead to eight equations, and two other equations are derived from the continuity of normal force, and the discontinuity of potential,  $4\pi inc\cos\theta$ , at the coil r=c. The equations are as usual linear, and their final solution is expressed most conveniently as follows:---

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$$\begin{split} \mathbf{P} &= 2(\mu-1)(\mu+2)(1/d^3-1/e^3)/\{9\,\mu+2(\mu-1)^2(1-d^3/e^3)\},\\ \mathbf{Q} &= (\mu-1)(2\,\mu+1)(b^3-a^3)/\{9\,\mu+2(\mu-1)^2(1-a^3/b^3)\}, \end{split}$$

both being positive, the transverse magnetic induction at  $\theta = 90^{\circ}$  is, at the inner surface of the inner shell.

$$B_{\text{max.}} = -\frac{12\pi i n \mu^2 (c^3 P + 2)}{(1 - PQ) \{9\mu + 2(\mu - 1)^2 (1 - d^3/c^3)^2\}}$$

and at the outer surface of the outer shell,

$$\mathrm{B_{max.}} = \frac{12\pi i n \mu^2 (2\,\mathrm{Q} + c^3)/c^3}{(1 - \mathrm{PQ})\{9\,\mu + 2\,(\mu - 1)^2\,(1 - d^3/c^3)\}}.$$

These may be taken as the average values across the sections of maximum, in the case of the shells to which our experiments relate, with an error of not more than about 3 per cent. In the special cases d=e, whence  $\Gamma=0$ , and a=b, whence Q=0, one shell is abolished, and the two previous solutions for a single shell are obtained. This solution is exact when the coil is wound indefinitely closely. It is of interest to calculate the numerical values in one special case for future comparison, and for this purpose we select the two largest shells used in the experiments, and referred to in the former paper as Nos. 3 and 4. Their permeabilities were practically identical, and  $\mu=148.5$ . The radii of the inner (No. 3) were 38.5 and 40.5 cm., and of the outer (No. 4) 42.5 and 44.5 cm. Let the coil be wound on the inner so that c=40.5 cm., then

$$\mu = 148.5$$
,  $\alpha = 38.5$ ,  $b = 40.5 = c$ ,  $d = 42.5$ ,  $c = 44.5$ ,

whence

P = 0.041055, Q = 54675, PQ = 0.5766, 
$$2 + c^3 P = 2.701$$
,  $(c^3 + 2Q)/e^3 = 1.995$ ,  $9\mu + 2(\mu - 1)^2(1 - d^3/e^3) = 7019.7$ ,

and therefore, when excited by a current i in n turns per unit diameter of a coil wound on the inner shell,  $B_{max}$  in the outer should be

$$B_{\text{max.}} = 558.0 in$$

on reduction, and in the inner,

$$B_{max} = -755.5 in.$$

their ratio being (inner)/(outer) = 1.345. The mutual action of the shells has thus changed the ratio from 1:2 to 3:4. The maxima are therefore more nearly equal than might have been anticipated, and, in the earlier experiments, a current used to demagnetise any one shell must have been almost equally effective in the case of the shell on the other side of the air

space containing the coil. Moreover, in the absence of the outer shell, the value of  $B_{max}$  produced in the inner may be shown to be

$$B_{\text{max.}} = 236 in,$$

so that its value is increased in the inner shell, by the presence of the outer, in the ratio 3.2:1. These results may be summarised as follows for this pair of shells:—

If a coil wound round the inner, in the absence of the outer, produces a value of  $B_{max}$ , equal to unity, then (1) if the inner is removed, and the outer placed round the coil,  $B_{max}$  in the outer is  $\frac{1}{2}$ , and (2) if both are present simultaneously,  $B_{max}$  in the inner is about 3.2, and in the outer is 2.4. We can deduce that in the demagnetisation of the entire set of shells in the original experiments, the application of currents of alternate signs simultaneously in all the coils must be at least six times as effective, for the second and third internal shells, as the successive application of these currents—a result which could hardly have been foreseen from general principles. Certain minor features in the curves then obtained can be interpreted on this basis.

These ratios necessarily become larger in the experiments described below, when all four shells are present simultaneously, and the current is passed through the coil on No. 3. But we do not include a detailed calculation of this case, which would be tedious. A discussion of one or two particular problems can be obtained somewhat simply, and, by comparison with experiment, will enable a determination to be made of the effect to which the theory may be vitiated by loose winding of the coils. We shall accordingly consider only this special problem to which the more interesting experiments relate.

Magnetising Coil applied to the Outermost of a Set of Four Shells.

The most important experiment—with reference to the testing of the theory in its ultimate application to the further shielding of the internal hollow of a set of four shells by the use of a magnetising current—is perhaps that in which the current is applied to a coil wound round the outer shell, whose value of  $B_{max}$  is tested by an exploring coil, as described later. The necessary calculation for this case is greatly facilitated by the use of the recurrence formulæ developed in the earlier paper,\* whose notation will be adopted without further description. The constant field in the hollow being  $u_1$ , calculation gives the following successive values of the functions u and v there described.

The mean radii of the four shells and air space form the sequence

- 30·5, 32·5, ..., 42·5, 44·5 cm.,
- \* 'Roy. Soc. Proc.,' A, vol. 92, p. 535 (1916).

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and the permeabilities, from inner to outer, are 82.4, 163, 148, 148.9—where fairly large error in the first, and a smaller error in the second, are of no importance. We then find, applying the recurrence formulæ without a rougher approximation than 1 per cent.,

$$\begin{array}{llll} \epsilon_1 = \frac{1}{3} \left\{ 1 - (30 \cdot 5/32 \cdot 5)^3 \right\} = 0 \cdot 0578, & \epsilon_{12} = \frac{1}{3} \left\{ 1 - (32 \cdot 5/34 \cdot 5)^3 \right\} = 0 \cdot 0547, \\ \epsilon_2 = 0 \cdot 0518, & \epsilon_{23} = 0 \cdot 0493, & \epsilon_3 = 0 \cdot 0470, & \epsilon_{34} = 0 \cdot 0449, \\ 2\mu_1 \dot{\epsilon}_1 \epsilon_{12} = 0 \cdot 5217, & 2\mu_2 \epsilon_2 \epsilon_{23} = 0 \cdot 8529, & 2\mu_3 \epsilon_3 \epsilon_{34} = 0 \cdot 6246, \\ 2\mu_1 \epsilon_1 = 9 \cdot 537, & 2\mu_2 \epsilon_2 = 17 \cdot 301, & 2\mu_3 \epsilon_3 = 13 \cdot 910, \\ \alpha_1 = 1 \cdot 4092, & \alpha_2 = 1 \cdot 7518, & \alpha_3 = 1 \cdot 5367, \\ \beta_1 = 0 \cdot 0547, & \beta_2 = 0 \cdot 0493, & \beta_3 = 0 \cdot 0449, \\ \gamma_1 = 8 \cdot 603, & \gamma_2 = 15 \cdot 694, & \gamma_3 = 12 \cdot 294, \\ \delta_1 = 0 \cdot 775, & \delta_2 = 0 \cdot 798, & \delta_3 = 0 \cdot 824. \end{array}$$

It is desirable that these intermediate functions should be placed on record for reference in future work on magnetic shielding, which is now in progress with these specimens of iron.

Again,

$$u_2/u_1 = 1.464,$$
  $r_2/v_1 = 9.378,$   $u_3/u_1 = 3.027,$   $r_3/v_1 = 30.46,$   $u_4/u_1 = 6.020,$   $v_4/v_1 = 62.32,$ 

and finally

$$v_4/u_4 = 10.35$$
,

relating to the air space just inside the fourth shell, on which the coil is wound. If the potential in the fourth shell is

$$\Omega = (Ar + B/r^2)\cos\theta$$

and its inner and outer radii are a and b, accordingly

$$\mu (A - 2B/a^3) = 10.35 (A + B/a^3),$$

giving the ratio of A to B, where  $\mu$  is its permeability. Application of the conditions at r = b and at the coil shows, moreover, that

$$-8\pi in = A(\mu+2)-2(\mu-1)B/b^3$$

so that A and B may be obtained. Thus in the outer shell,

$$B_{\text{max.}} = \mu \left( A + B/b^3 \right) = -\frac{8 \pi i n \mu \left\{ 1 + \left[ (\mu - 10.35)/(2 \mu + 10.35) \right] a^3/b^3 \right\}}{\mu + 2 - 2 (\mu - 1) \left[ (\mu - 10.35)/(2 \mu + 10.35) \right] a^3/b^3}$$

with a = 42.5, b = 44.5  $\mu = 148.9$ ,

$$B_{max} = 148.7 in.$$

If the current is in ampères, division by 10 is necessary in order to obtain the value in C.G.S. units.

If  $n = \frac{1}{2}$ , or half a turn per continetre of diameter, were a sufficiently

close winding to render the formulæ exact, a current of 1 ampère should give the experimental value

$$B_{\text{max.}} = 14.87/2 = 7.43 \text{ C.G.S. units}$$

for the outer shell when examined by an exploring coil.

Returning to the recurrence formulæ, we notice that  $v_3/u_8 = 10 \cdot 06$ . This result enables us to correct the previous formula, applicable to a coil wound between the third and fourth shells, for the presence of the other two shells in the interior. For, in that formula, the function P remains unaltered and the only effect of the two inner shells is to alter Q, which becomes

$$Q = \frac{a^{8} \{(\mu - 1)[(2\mu + 10.06)/(\mu - 10.06)]b^{3}/a^{3} - (2\mu + 1)\}}{(\mu + 2)[(2\mu + 10.06)/(\mu - 10.06)]b^{3}/a^{3} - 2(\mu - 1)}$$

instead of its original value in the former calculation, which was

$$\mathbf{Q} = (\mu - 1)(2\mu + 1)(b^3 - a^3)/\{9\mu + 2(\mu - 1)^2(1 - a^3/b^3)\}.$$

The rest of the formula is as before, and  $(a, b, \mu)$  refer to the third shell. The numerical value of Q in the present case is found to be Q = 58,908, corresponding to a = 38.5, b = 40.5,  $\mu = 148.9$ , and thus

$$(c^3 + 2Q)/c^3 = 2.090, 1 - PQ = 0.3785,$$

and, finally, for a coil carrying a current i, wound round the third of a set of four shells of the present constants,  $B_{max}$  in the outer is given by

$$B_{max} = 653.9 in$$

or 65·39 in, if the current is in ampères. For  $n=\frac{1}{2}$ , the value per ampère of current is 32·69 C.G.S. units. A comparison with a direct experiment is made later. In the meantime, it is instructive to notice that, in the absence of the two inner shells,  $B_{max}$  for the fourth shell when the third is wound was calculated previously as 558 in. The inner shells have raised its value in the ratio 13:11—a much smaller mutual effect is involved, as might be expected, owing to the shielding influence of the third shell.

The four shells remained, throughout the experiments, set up concentrically, each being wound with a magnetising coil, and the axis of all the coils was the diameter coinciding with the direction of the earth's field. The value of n was in each case  $\frac{1}{2}$ , the number of turns wound on the shells being respectively 34, 38, 42, and 46. The various dimensions have been specified already, and the shells are formed from high permeability magnet steel. Since the previous experiments were made, the butting surfaces of all the shells have been machined in such a manner that each of the two halves of any

original shell penetrates the other. Preliminary tests, not described in this paper, have indicated that the leakage originally present on account of this lack of machining has almost entirely disappeared, so that the theoretical formulæ are strictly applicable if the coils are sufficiently closely wound.

The four concentric shells were placed with their junction planes at right angles to the direction of the earth's magnetic field, and therefore parallel to the plane of any winding of a coil. The exploring coil layin a plane parallel also to these junction planes, and distant about 7 cm. from the junction plane of the fourth shell. It surrounded the iron of the outermost shell, referred to as No. 4, and consisted of one complete turn of insulated copper wire touching the outside of the shell, and one complete turn touching also the inside. The ends of the inside turn were brought out of the shell through a small hole in the junction plane, by bending the two ends, which are now stranded together, at right angles to the plane of the coil and then threading them through the The inside and outside turns were then placed in series so that the coil completely surrounded the iron once. The section of the effective part of the coil is thus a plane annulus whose radii are practically those of the outermost shell, and the coil is cut normally, in view of its parallelism to the magnetising coils, by the transverse magnetic induction at  $\theta = \pi/2$  in the outer shell, over the whole area of section of that shell. The normal induction across the coil is thus the product of the sectional area  $\pi(r_1^2-r_2^2)$ , where  $r_2$ and  $r_1$  are the radii 42.5, 44.5 cm., of the outer shell, and the average value of  $B_{max}$ , for the outer shell as calculated already.

More strictly, this product should be multiplied by a magnitude of the order  $\cos 10^\circ$ , on account of the small displacement 7 cm. of the plane of the exploring coil from the diametral plane  $\theta=\pi/2$ . But this would only make a change not exceeding 2 per cent. The exact position of the exploring coil was so chosen that, while giving B with this degree of accuracy on one ground, it should at the same time be so far removed from the junction that the effect of any small air space should be negligible. For although the two hemispheres constituting the whole shell were dovetailed together, the degree of fit was not sufficient to ensure perfect contact throughout. A very small air space does in fact still exist, and we may therefore assume that the observed magnetic induction might on this account be slightly smaller than the calculated value even in the ideal state of packing of the magnetising coils.

The resistance of the exploring coil was quite negligible in comparison with that of the ballistic galvanometer. This instrument, which was of the d'Arsonval type, had a resistance of 467 ohms at 10° C.; to this additional resistance was added in order to obtain the sensibility necessary to ensure

that the deflection was not of a magnitude capable of serious error on account of permanent set in the suspending fibre. Let R be the resistance of the circuit of galvanometer, exploring coil, and extra resistance when this was used, and T the periodic time of the swinging coil of the instrument, in which a steady current of C ampères produces a deflection  $\alpha$ . Let 1+r be the ratio of two successive deflections of the galvanometer coil when on open circuit. Then if m is the number of turns in the exploring coil, A the area of cross-section of the iron in the plane of the exploring coil, in square centimetres, and  $\Delta$  the mean of the first and second deflections obtained by reversal of the current in the magnetising coil, we can deduce\* the formula:—

$$B_{\text{max.}} = (1 + r/2) \left( \text{CT} / 2\pi\alpha \right) \left( \text{R}\Delta / 2m\text{A} \right) \times 10^8.$$

The following values of the constants were obtained as the result of a calibration of the instrument and shell:—

$$1+r/2 = 1.03$$
,  $C/\alpha = 0.685 \times 10^{-9}$ ,  $T = 8.15$  sec.  $A = 562$  sq. cm.

with m = 1. Throughout the experiments, double deflections were observed on a scale having  $\frac{1}{2}$  mm. divisions at a distance of 1340 mm. from the mirror.

The decrement factor 1+r/2 was used so long as it did not exceed 1.03. But the resistance of the exploring coil is so small in comparison with that of the galvanometer that, when no extra resistance is inserted in the circuit, the galvanometer is short-circuited when used for observing deflections produced by reversal of current in a magnetising coil. Under these circumstances the decrement is very much greater, and the spot of light, after the first throw, returns to zero and gives a relatively small deflection on the other side. The ordinary treatment of damping is not then applicable. But we notice that failure to correct for a damping factor 1.03 only introduces an error of about 3 per cent., and this occurs in practice in our experiments when a resistance of 10,000 ohms is added. The interpretation of readings with smaller resistances added can be found by a preliminary experiment, which was made as follows:—

The third magnetising coil, wound between the two outermost shells, was used and a current of 198 ampères passed through it. Deflections were observed with varied additional resistances in the circuit of the exploring coil. Reversal of current in the magnetising coil in every case produces the same value of  $B_{\text{max}}$  in the fourth shell, and therefore the same induced electromotive force in the exploring circuit. The product of deflection and total resistance should therefore be the same in every case, if the damping factors

<sup>\*</sup> See, e.g., 'Phil. Trans.,' A, vol. 180, p. 445 (1889).

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are identical. This product may be taken as correct with 10,000 ohms added to the resistance of the galvanometer, and thence the true deflection, in the absence of damping, calculated in the other cases. The interpretation of a reading with any added resistance may then be obtained by interpolation. This method has the advantage of assuming no theory of the abnormal damping.

The results are shown in the annexed Table:—

Total resistance (ohms).	First swing.	(Product)/100.	Proportional increase necessary for coincidence
10,467	80	8,384	1
5,467	148	8,110	1 .03
1,467	428	6,884	1.82
967	566	5,547	1 .21
467	804	3,859	2 ·17

Table I.—Variation of Damping with Resistance.

If 1.03 is multiplied by the value in the last column, we get a practical determination of the decrement factor, independently of any theory, and valid even for the enormous factor which occurs with no added resistance. Interpolation is not in fact necessary, for all the experiments later are performed with added resistances of 0, 1000, or 10,000 ohms. In the experiments of the earlier paper, large resistances were always used, so that no discussion of abnormal damping was then necessary. Thus any first swing with 0, 1000, 10,000 ohms added resistance must be multiplied by the factors (1.03)(2.17, 1.32, 1), or 2.23, 1.36, 1.03 respectively, in order to obtain the undamped reading. We do not attempt to discuss any theory as to the origin of these values, for it constitutes an independent problem of some difficulty, and is not strictly relevant to the present paper.

#### Experimental Results.

The values of B<sub>max</sub>, have been determined in the following cases:-

- (a) The four shells were set up as described, and the readings taken in correspondence with various currents in the magnetising coil on the third shell, the exploring coil being on the fourth shell.
- (b) Similar readings were taken when the system was excited instead by the magnetising coil on the fourth shell.

The values of  $B_{\text{max}}$  were obtained in accordance with the discussion in the preceding section, and are shown in the subjoined Tables II and III.

Current in ampères.	Deflection in scale divisions.	Added resistance in ohms.	B <sub>max</sub> . in C.G.S. units.	B <sub>max</sub> ./curren
0 .0327	9	0	0 .752	23 .0
0 ·109	36	0	2 .97	27 .2
0 .262	. 90	0	7 -42	28.8
0 .436	169	0	13 .9	31 .9
0 .785	. 325	0	26 .8	34 1
1 .8	280	1,000	45 .9	35 .3
2 ·1	90	10,000	76 ·8	86 .5
3 .32	167	10,000	143	47 6
5 · 5	317	10,000	272	49 4

Table II.—Magnetising Coil on the Third Shell.

Table III.—Magnetising Coil on Fourth Shell.

Current in ampères.	Deflection in scale divisions.	Added resistance in ohms.	B <sub>max</sub> . in C.G.S. units.	B <sub>max</sub> ./curre
0.12	11	o	0 .908	7 .16
0.41	41	0	3 ·38	8 .2
0.714	78	0	6 .44	9:10
5 ·1	58	10,000	49 .5	9.7
7 ·1	82	10,000	70.0	9.9

#### Discussion.

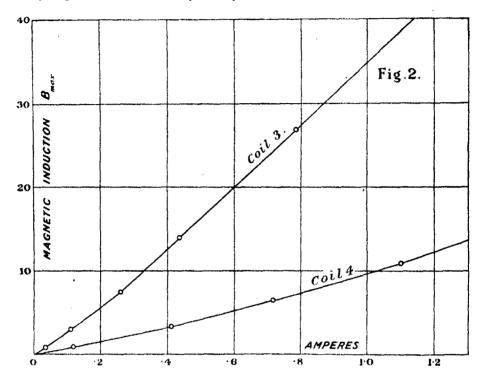
The graphs shown in fig. 2 indicate also the results of these experiments. For small values of the currents, they are very closely represented by straight lines, as would be expected. The effect of the curve of magnetisation then comes into play, so that, although, on account of loose winding of the coil; the values of  $B_{\text{max.}}$ /current are initially smaller than those predicted on theoretical grounds, they ultimately become larger than those calculated on the assumption of constant permeabilities of the shells, and the graphs become more parabolic.

The calculations of an earlier section indicate that, if the permeabilities were constant,  $B_{\text{max}}$ /current should be equal to 32.7 when the third magnetising coil is used, and 7.4 when the current is passed through the fourth. For the smaller values of the current, the values of  $B_{\text{max}}$  may be expected, in view of the curve of magnetisation, to follow the empirical law,

$$B_{\text{max.}} = i(A + Bi)$$

where i is the current, at least roughly, although the constant B would have no simple physical meaning on account of the different magnetising forces on the various shells which shield one another. For currents i = 0.1 to i=1.3 ampères, the average value of A is 31.4, neglecting the reading

corresponding to i = 0.03, in which an error of a scale division would be very important. This is very nearly the theoretical value, but is high on



account of initial slope of the magnetisation curve. We may take  $27\cdot2$  as the true value of A very closely, when  $i=0\cdot1$  ampère. The first four readings may be fitted into the formula

$$B_{\text{max}} = i(26.2 + 10i),$$

with errors in  $B_{\rm max}/i$  of magnitudes +0.1, -0.5, -1.3, -0.1. The later values require an extra term in the empirical formula, but for the currents of this order, only a very small experimental error not exceeding about 3 per cent is indicated. Small magnetic inductions can thus be measured with extreme accuracy by this method of the exploring coil. The limiting value of the ratio with the present magnetising coil is evidently about 26.2 instead of 32.7, showing that Maxwell's formula involves a considerable error when applied to a coil even so closely wound as the present one, when the iron of the core is near the coil. At the same time, the data are now available for future use of these coils, and the need for a theoretical investigation of a loosely wound coil, which has been prominent for some time, without any solution, is removed. The Table for the coil on the fourth

shell exhibits the same general characteristics, and calls for no further remarks.

Perhaps one of the most interesting problems opened up by the present investigation is an enquiry into the limit to which demagnetisation of a shell can be carried. It would be necessary, for certain types of previous magnetic history of the iron, to apply reversals of a continually diminishing force, which began with a value corresponding to maximum permeability, as shown on the (BH) curve of the material. This would be difficult, on account of the necessary magnitude of the current for an arrangement of shells such as the present, which, however, as shown in the earlier paper,\* is that of maximum shielding for a large space. Since effective demagnetisation, or, at least, the production of uniformity in the internal field of the central hollow, is a necessary preliminary to the removal of that residual field by the application of currents, the problem is of some importance. But at this point it is sufficient to indicate the necessity for a determination of what constitutes "effective demagnetisation."

#### Induced Currents.

The reversal of magnetisation within undivided iron magnet cores has been studied to a great extent on its experimental side, and it is known that the induced currents in the iron continue for a considerable time, and tend to maintain the magnetisation in its condition preceding the reversal. When a ballistic galvanometer is used in combination with an exploring coil wound on such magnets, the deflections of the instrument do not give the complete change of magnetic induction; the effect is similar to the damping caused by connecting a resistance across the terminals of the instrument. A continued current in one direction, caused by the slow change of magnetisation, gives rise to a first deflection considerably greater than the second—in the opposite direction—and the third deflection may exceed the second.

So far as we are aware, the lowest forces at which the delay caused by induced currents in large masses has been examined, are 1.7† and 1.2‡ in C.G.S. units. In the first case the magnet was of wrought iron of diameter 10.16 cm. (4 inches), and in the second, of dynamo magnet steel of diameter 30.5 cm. (12 inches). Changes at the centre of the core were observed 46 seconds after reversal in the former case and 400 seconds in the latter. The experiments showed, moreover, that, with small forces of this order of

<sup>\* &#</sup>x27;Roy. Soc. Proc.,' A, vol. 92, p. 529 (1916).

<sup>† &#</sup>x27;Phil. Trans.,' A, vol. 186, p. 93 (1895).

<sup>1 &#</sup>x27;Journ. Inst. Elec. Eng.,' Pt. 116, vol. 24, p. 194.

magnitude, there is but a single maximum rate of change of the magnetic induction, which occurs at a comparatively early stage.

But the values of the magnetic induction corresponding to these forces were of the orders 7000 and 5000 C.G.S. units. In the experiments of the present communication, the magnetic induction in the outermost shell is only 67.6 C.G.S. units when a current of 7 ampères is used in its magnetising coil. Corresponding to a current of 5.5 ampères in the coil wound on the third shell, the maximum transverse induction in the fourth or outermost shell is 272 C.G.S. units. These currents have not as yet been greatly exceeded in our experiments on demagnetisation. It is interesting, and of some importance, to enquire whether the delay caused by the reversal of such small inductions is sufficiently great to affect the decrement, as ordinarily obtained, of the readings of a galvanometer whose periodic time is 8 seconds.

Some experiments have been made in order to test this point. A list of deflections due to a reversal of a current in the third coil, and its corresponding effect on an exploring coil wound on the fourth shell, has been used already for another purpose. The same arrangement, with a current of 1.98 ampères reversed, and various additional resistances inserted in the galvanometer circuit, was used also in determining the ratio of first to second deflection corresponding to each resistance. The exploring coil was then cut out of the galvanometer circuit, and deflections were observed corresponding to the same resistances as before, ranging from 0 to 10,000 ohms, when the coil of the galvanometer was initially set in motion by a primary cell of low voltage working through a very high resistance, the battery circuit being open while the readings were taken. The ratios of first to second deflection were again calculated, and the comparison is made in Table IV.

Table IV.

Additional non-inductive resistance in galvanometer circuit.	Deflection ratio when caused by exploring coil constantly in circuit.	Deflection ratio when coil of galvanometer is set in motion by primary cell.
ohms.		
10,000	1 '08	1 .10
5,000	1 .29	1 .29
1,000	2 · 27	2 .25
500	8 .50	3 .68
0	19 8	57 -4

When the additional resistance was zero, or in short circuit, the second deflection was so small as to render the ratio very uncertain. But the ratios

corresponding to other resistances are in such close agreement that the delay in the change due to eddy currents must be effectively negligible. This result is of some importance, for it might have been inferred from the earlier experiments that a considerable delay was possible in a shell of thickness 2 cm. The argument would be applied as follows:—

In the distribution of induced currents in its mass a plate is comparable with a wire whose diameter is twice the thickness of the plate (loc. cit.). The time required to effect a complete reversal of any value of the magnetic induction in one of our shells should be of the same order as in a cylinder of diameter 4 cm. In two cylinders of different diameters, each subjected to the reversal of the same magnetic force, similar magnetic events will happen, but at times proportional to the squares of the diameters. Comparing therefore a solid shell of thickness 2 cm. with the solid magnet of diameter 10 cm., mentioned in the earlier experiments, the delay in the shell would be of order  $46 \times (4/10)^2 = 7.4$  seconds. Comparison with the magnet of diameter 30 cm. gives  $400 \times (4/30)^2 = 7.1$  seconds.

It is evident that if the induced currents are to disappear when the magnetic induction is of the order 6000, a considerable time must elapse between successive reversals of the magnetising force in this process of demagnetisation by reversal and diminution. But the present experiments show that for magnetic inductions not exceeding 300 C.G.S. units this necessary time interval is greatly reduced, for the delay due to induced currents is negligible in comparison with such a time as 8 seconds, the periodic time of the ballistic galvanometer employed. This has important implications in connection with work at high frequencies,

#### Summary.

- (1) The paper contains a solution of certain problems which arise in the production of an effective magnetic shield for large spaces. These relate mainly to the effective demagnetisation of the shells of which the shield is constituted.
- (2) Theoretical solutions of problems relating to the effects of indefinitely closely wound coils on various shells of such a shield are given, and compared with the experimental values for an actual coil, as determined by an exploring coil and ballistic galvanometer.
- (3) The experiments supply an estimate of the deviations of Maxwell's formula, for the field inside a spherically wound helical wire, from the true values, when the spacing in the helix is of importance.

(4) A study of the necessary interval between current reversals in the process of demagnetisation has been made, and it is shown that the delay in reversal of magnetic phenomena in considerable masses of iron, due to eddy currents, is extremely small when the magnetic inductions are less than 300 C.G.S. units.

# On the Dynamics of Revolving Fluids. By LORD RAYLEIGH, O.M., F.R.S.

(Received December 8, 1916.)

So much of meteorology depends ultimately upon the dynamics of revolving fluid that it is desirable to formulate as clearly as possible such simple conclusions as are within our reach, in the hope that they may assist our judgment when an exact analysis seems impracticable. An important contribution to this subject is that recently published by Dr. Aitken.\* It formed the starting point of part of the investigation which follows, but I ought perhaps to add that I do not share Dr. Aitken's views in all respects. His paper should be studied by all interested in these questions.

As regards the present contribution to the theory it may be well to premise that the limitation to symmetry round an axis is imposed throughout.

The motion of an inviscid fluid is governed by equations of which the first expressed by rectangular co-ordinates may be written

$$\frac{du'}{dt} + u'\frac{du'}{dx} + v'\frac{du'}{dy} + w'\frac{du'}{dz} = -\frac{dP}{dx},\tag{1}$$

where

$$P = \int dp/\rho - V, \qquad (2)$$

and V is the potential of extraneous forces. In (2) the density  $\rho$  is either a constant, as for an incompressible fluid, or at any rate a known function of the pressure p. Referred to cylindrical co-ordinates r,  $\theta$ , z, with velocities u, v, w, reckoned respectively in the directions of r,  $\theta$ , z increasing, these equations become

$$\frac{du}{dt} + u\frac{du}{dr} + v\left(\frac{du}{rd\theta} - \frac{v}{r}\right) + w\frac{du}{dz} = -\frac{dP}{dr},\tag{3}$$

<sup>\* &</sup>quot;The Dynamics of Cyclones and Anticyclones.—Part 3," 'Roy. Soc. Edin. Proc., vol. 36, p. 174 (1916).

<sup>†</sup> Compare Basset's 'Hydrodynamics,' § 19.

$$\frac{dv}{dt} + u\frac{dv}{dr} + v\left(\frac{dv}{rd\theta} + \frac{u}{r}\right) + w\frac{dv}{dz} = -\frac{dP}{rd\theta},$$
 (4)

$$\frac{dw}{dt} + u\frac{dw}{dr} + v\frac{dw}{rd\theta} + w\frac{dw}{dz} = -\frac{dP}{dz}.$$
 (5)

For the present purpose we assume symmetry with respect to the axis of z, so that u, v, w, and P (assumed to be single-valued) are independent of  $\theta$ . So simplified, the equations become

$$\frac{du}{dt} + u\frac{du}{dx} - \frac{v^2}{x} + w\frac{du}{dz} = -\frac{d\mathbf{P}}{dx},\tag{6}$$

$$\frac{dv}{dt} + u\frac{dv}{dz} + \frac{uv}{x} + w\frac{dv}{dz} = 0, (7)$$

$$\frac{dw}{dt} + u\frac{dw}{dr} + w\frac{dw}{dz} = -\frac{dP}{dz},\tag{8}$$

of which the second may be written

$$\left(\frac{d}{dt} + u\frac{d}{dr} + w\frac{d}{dz}\right)(rv) = 0,$$
(9)

signifying that (rv) may be considered to move with the fluid, in accordance with Kelvin's general theorem respecting "circulation." If  $r_0$ ,  $v_0$ , be the initial values of r, v, for any particle of the fluid, the value of v at any future time when the particle is at a distance r from the axis is given by  $rv = r_0v_0$ .

Respecting the motion expressed by u, w, we see that it is the same as might take place with v = 0, that is when the whole motion is in planes passing through the axis, provided that we introduce a force along r equal to  $v^2/r$ . We have here the familiar idea of "centrifugal force," and the conclusion might have been arrived at immediately, at any rate in the case where there is no (u, w) motion.

It will be well to consider this case (u = 0, w = 0) more in detail. The third equation (8) shows that P is then independent of z, that is a function of r (and t) only. It follows from the first equation (6) that v also is a function of r only, and  $P = \int r^2 dr/r$ . Accordingly by (2)

$$\int dp/\rho = V + \int v^2 r^{-1} dr. \tag{10}$$

If V, the potential of impressed forces, is independent of z, so also will be p and  $\rho$ , but not otherwise. For example, if gravity (g) act parallel to z (measured downwards),

$$\int dp/\rho = C + gz + \int v^2 dr/r, \qquad (11)$$

gravity and centrifugal force contributing independently. In (11)  $\rho$  will be

constant if the fluid is incompressible. For gases following Boyle's law  $(p = u^2 \rho)$ ,  $a^2 (\log \rho)$ , or  $\log p = C + gz + (v^2 dr/r)$ . (12)

At a constant level the pressure diminishes as we pass inwards. But the corresponding rarefaction experienced by a compressible fluid does not cause such fluid to ascend. The heavier part outside is prevented from coming in below to take its place by the centrifugal force.\*

The condition for equilibrium, taken by itself, still leaves v an arbitrary function of r, but it does not follow that the equilibrium is stable. In like manner an incompressible liquid of variable density is in equilibrium under gravity when arranged in horizontal strata of constant density, but stability requires that the density of the strata everywhere increase as we pass downwards. This analogy is, indeed, very helpful for our present purpose. As the fluid moves (u and w finite) in accordance with equations (6), (7), (8), (vr) remains constant (k) for a ring consisting always of the same matter, and  $v^2/r = k^2/r^3$ , so that the centrifugal force acting upon a given portion of the fluid is inversely as  $r^3$ , and thus a known function of position. The only difference between this case and that of an incompressible fluid of variable density, moving under extraneous forces derived from a potential, is that here the inertia concerned in the (u, w) motion is uniform, whereas in a variably dense fluid moving under gravity, or similar forces, the inertia and the weight are proportional. As regards the question of stability, the difference is immaterial, and we may conclude that the equilibrium of fluid revolving one way round in cylindrical layers and included between coaxial cylindrical walls is stable only under the condition that the circulation (k) always increases with r. In any portion where k is constant, so that the motion is there "irrotational," the equilibrium is neutral.

An important particular case is that of fluid moving between an inner cylinder (r=a) revolving with angular velocity  $\omega$  and an outer fixed cylinder (r=b). In the absence of viscosity the rotation of the cylinder is without effect. But if the fluid were viscous, equilibrium would require

$$k = vr = a^2 \omega (b^2 - r^2)/(b^2 - a^2),$$

expressing that the circulation diminishes outwards. Accordingly a fluid without viscosity cannot stably move in this manner. On the other hand, if it be the outer cylinder that rotates while the inner is at rest,

$$k = vr = b^2 \omega (r^2 - a^2) / (b^2 - a^2),$$

and the motion of an inviscid fluid according to this law would be stable.

- \* When the fluid is viscous the loss of circulation near the bottom of the containing vessel modifies this conclusion, as explained by James Thomson.
  - † Lamb's 'Hydrodynamics,' § 333.

We may also found our argument upon a direct consideration of the kinetic energy (T) of the motion. For T is proportional to  $\int v^2 dr$ , or  $\int k^2 dr^2/r^2$ . Suppose now that two rings of fluid, one with  $k = k_1$  and  $r = r_1$  and the other with  $k = k_2$  and  $r = r_2$ , where  $r_2 > r_1$ , and of equal areas  $dr_1^2$  or  $dr_2^2$  are interchanged. The corresponding increment in T is represented by

 $(dr_1^2 = dr_2^2)\{k_2^2/r_1^2 + k_1^2/r_2^2 - k_1^2/r_1^2 - k_2^2/r_2^2\} = dr^2(k_2^2 - k_1^2)(r_1^{-2} - r_2^{-2}),$  and is positive if  $k_2^2 > k_1^2$ ; so that a circulation always increasing outwards makes T a minimum and thus ensures stability.

The conclusion above arrived at may appear to conflict with that of Kelvin,\* who finds as the condition of minimum energy that the vorticity, proportional to  $r^{-1}dk/dr$ , must increase outwards. Suppose, for instance, that  $k = r^{4}$ , increasing outwards, while  $r^{-1}dk/dr$  decreases. But it would seem that the variations contemplated differ. As an example, Kelvin gives for maximum energy

$$v = r$$
 from  $r = 0$  to  $r = b$ ,  
 $v = b^2/r$  from  $r = b$  to  $r = a$ ;

and for minimum energy

$$v = 0$$
 from  $r = 0$  to  $r = \sqrt{(a^2 - b^2)}$ ,  
 $v = r - (a^2 - b^2)/r$  from  $r = \sqrt{(a^2 - b^2)}$  to  $r = a$ .  
 $v = a = \int_0^a v r^2 dr = \frac{1}{4}b^2(2a^2 - b^2)$ ,

In the first case

and in the second case

$$\int_0^a vr^2 dr = \frac{1}{4}b^2;$$

so that the moment of momentum differs in the two cases. In fact Kelvin supposes operations upon the boundary which alter the moment of momentum. On the other hand, he maintains the strictly two-dimensional character of the admissible variations. In the problem that I have considered, symmetry round the axis is maintained and there can be no alteration in the moment of momentum, since the cylindrical walls are fixed. But the variations by which the passage from one two-dimensional condition to another may be effected are not themselves two-dimensional.

The above reasoning suffices to fix the criterion for stable equilibrium; but, of course, there can be no actual transition from a configuration of unstable equilibrium to that of permanent stable equilibrium without dissipative forces, any more than there could be in the case of a heterogeneous liquid under gravity. The difference is that in the latter case dissipative

<sup>\* &#</sup>x27;Nature.' vol. 23, October, 1880; 'Collected Papers,' vol. 4, p. 175.

forces exist in any real fluid, so that the fluid ultimately settles down into stable equilibrium, it may be after many oscillations. In the present problem ordinary viscosity does not meet the requirements, as it would interfere with the constancy of the circulation of given rings of fluid on which our reasoning depends. But for purely theoretical purposes there is no inconsistency in supposing the (u, w) motion resisted while the the v-motion is unresisted.

The next supposition to u = 0, w = 0 in order of simplicity is that u is a function of r and t only, and that w = 0, or at most a finite constant. It follows from (8) that P is independent of z, while (6) becomes

$$\frac{du}{dt} + u\frac{du}{dr} - \frac{v^2}{r} = -\frac{dP}{dr},\tag{13}$$

determining the pressure. In the case of an incompressible fluid u as a function of r is determined by the equation of continuity ur = C, where C is a function of t only; and when u and the initial circumstances are known, v follows. As the motion is now two-dimensional, it may conveniently be expressed by means of the vorticity  $\zeta$ , which moves with the fluid, and the stream-function  $\psi$ , connected with  $\zeta$  by the equation

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{d\mathbf{\psi}}{dr}\right) + \frac{1}{r^2}\frac{d^2\mathbf{\psi}}{d\theta^2} = 2\zeta. \tag{14}$$

The solution, appropriate to our purpose, is

$$\Psi = 2 \left[ dr \, r^{-1} \right] \zeta r dr + A \log r + B\theta, \tag{15}$$

where A and B are arbitrary constants of integration. Accordingly

$$u = \frac{d\psi}{rd\theta} = \frac{B}{r}, \qquad v = \frac{d\psi}{dr} = \frac{2}{r} \left( \zeta r dr + \frac{A}{r} \right).$$
 (16)

In general, A and B are functions of the time, and  $\zeta$  is a function of the time as well as of r.

A simple particular case is when  $\zeta$  is initially, and therefore permanently, uniform throughout the fluid. Then

$$v = \zeta r + \Lambda r^{-1}. \tag{17}$$

Let us further suppose that initially the motion is one of pure rotation, as of a solid body, so that initially A = 0, and that then the outer wall closes in. If the outer radius be initially  $R_0$  and at time t equal to R, then at time t

$$A = \zeta(R_0^2 - R^2),$$
 (18)

<sup>\*</sup> It may be remarked that (17) is still applicable under appropriate boundary conditions even when the fluid is viscous.

since vr remains unchanged for a given ring of the fluid; and correspondingly,

$$v = \xi \{r + (R_0^2 - R^2) r^{-1}\}. \tag{19}$$

Thus, in addition to the motion as of a solid body, the fluid acquires that of a simple vortex of intensity increasing as R diminishes.

If at any stage the u motion ceases, (6) gives

$$dp/dr = \rho v^2/r, (20)$$

and thus

$$p/\rho = \zeta^2 \{ \frac{1}{2} r^2 + 2(R_0^2 - R^2) \log r - \frac{1}{2} (R_0^2 - R^2)^2 r^{-2} \} + \text{const.}$$
 (21)

Since, as a function of r,  $v^2$  continually increases as R diminishes, the same is true for the difference of pressures at two given values of r, say  $r_1$  and  $r_2$ , where  $r_2 > r_1$ . Hence, if the pressure be supposed constant at  $r_1$ , it must continually increase at  $r_2$ .

If the fluid be supposed to be contained between two coaxial cylindrical walls, both walls must move inwards together, and the process comes to an end when the inner wall reaches the axis. But we are not obliged to imagine an inner wall, or, indeed, any wall. The fluid passing inwards at  $r = r_1$  may be supposed to be removed. And it remains true that, if it there pass at a constant pressure, the pressure at  $r = r_2$  must continually increase. If this pressure has a limit, the inwards flow must cease.

It would be of interest to calculate some case in which the (u, w) motion is less simple, for instance, when fluid is removed at a point instead of uniformly along an axis, or inner cylindrical boundary. But this seems hardly practicable. The condition by which v is determined requires the expression of the motion of individual particles, as in the so-called Lagrangian method, and this usually presents great difficulties. We may however, formulate certain conclusions of a general character.

When the (u, w) motion is slow relatively to the v motion, a kind of "equilibrium theory" approximately meets the case, much as when the slow motion under gravity of a variably dense liquid retains as far as possible the horizontal stratification. Thus oil standing over water is drawn off by a syphon without much disturbing the water underneath. When the density varies continuously the situation is more delicate, but the tendency is for the syphon to draw from the horizontal stratum at which it opens. Or if the liquid escapes slowly through an aperture in the bottom of the containing vessel, only the lower strata are disturbed. In like manner when revolving fluid is drawn off in the neighbourhood of a point situated on the axis of rotation, there is a tendency for the surfaces of constant circulation to remain

cylindrical and the tendency is the more decided the greater the rapidity of rotation. The escaping liquid is drawn always from along the axis and not symmetrically in all directions, as when there is no rotation. The above is, in substance, the reasoning of Mr. Aitken, who has also described a simple experiment in illustration.

P.S.—It may have been observed that according to what has been said above the stability of fluid motion in cylindrical strata requires only that the square of the circulation increase outwards. If the circulation be in both directions, this disposition involves discontinuities, and the stability exists only under the condition that symmetry with respect to the axis is rigorously maintained. If this limitation be dispensed with, the motion is certainly unstable, and thus the stability of motion in cylindrical layers really requires that the circulation be one-signed. On the general question of the two-dimensional motion of liquids between fixed co-axial cylindrical walls reference may be made to a former paper.\* The motion in cylindrical strata is stable provided that the "rotation either continually increase or continually decrease in passing outwards from the axis." The demonstration is on the same lines as there set out for plane strata.

<sup>\* &#</sup>x27;Proc. Lond. Math. Soc.,' vol. 11, p. 57 (1880); 'Scientific Papers,' vol. 1, p. 487. See last paragraph.

- A Determination of the Heat of Vaporisation of Water at 100° C. and One Atmosphere Pressure in Terms of the Mean Calorie.
  - By T. Carlton-Sutton, B.Sc., Government Research Scholar in the . University of Melbourne, 1914-15.

(Communicated by Principal E. H. Griffiths, F.R.S. Received August 1, 1916.)

#### A .- Introduction.

The value of the latent heat of vaporisation of water at 100° C. and one atmosphere pressure is here measured directly in terms of the mean calorie by using a steam calorimeter that may be regarded as a development of Joly's classical apparatus. It is claimed that a high degree of accuracy has been attained on account of—

- (1) An ice-bath that remains steady for one or two hours;
- (2) A shielding device, by means of which a damp body can be left hanging in a steam chamber without loss or gain in weight; and
  - (3) A determination of the effect of the dampness of the steam.

#### B.—THEORY OF THE METHOD.

The temperature of a bulb of thermal capacity K is raised from the freezing point  $\theta$  to the boiling point  $\Theta$  by surrounding it with steam, a mass m of steam being condensed on the bulb, where

$$K(\Theta - \theta) = mL$$

The bulb is then filled with water (of mass M) and the process repeated, a mass m' of steam being condensed, where, omitting small corrections,

$$(K + Ms)(\Theta - \theta) = m'L$$

whence

$$L = \frac{Ms}{m' - m} (\Theta - \theta),$$

i.e., the heat of vaporisation is measurable in appropriate calories (s = 1) in terms of a temperature difference and the ratio of the masses M and (m'-m).

## CI. Outline of Apparatus.

The apparatus, as shown in the diagrams (figs. 1-3), consists of—

A balance, from one arm of which is suspended a windlass, W. This raises and lowers the bulb and pan, B, P. These may be raised into the VOL. XCIII.—A.

chamber 1, or lowered into the chilling vessel 2, or the steam bath 3, either of which may be attached directly beneath 1.

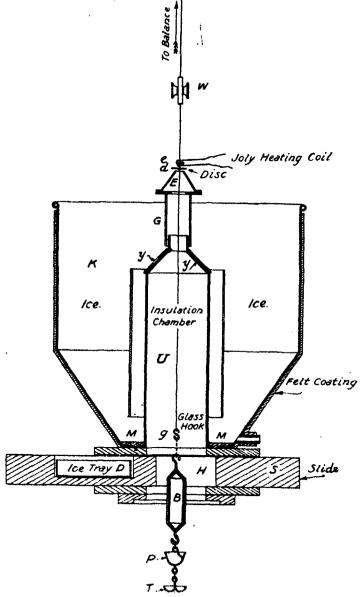
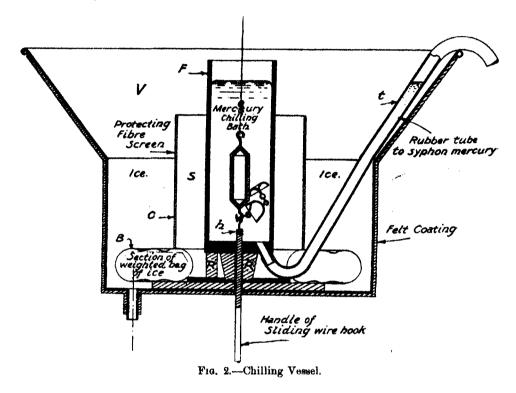


Fig. 1.—Thick lines = Sections of Conductors; Shaded lines = Sections of Insulators,

2. A cast brass vessel, 1, of the shape shown, surrounded by an insulating felt jacket. Attached to the bottom of the vessel are insulating blocks,

through which passes an insulating slide S, containing a depression D, and a circular hole H. The space K is filled with ice to the level of the glass tube G, and the slide is placed so that the depression D (containing a dish of ice) is brought directly below the inner chamber U of the vessel 1, and closes it. The walls, floor, and top of that chamber are then at 0° C, and a bulb enclosed therein, if initially at 0° C, will remain at that temperature indefinitely. When the slide is moved so that the circular hole H is directly



below the inner chamber U, the latter is placed in communication with the vessel attached below, which may be either the chilling chamber 2 or the steam chamber 3.

- 3. A chilling chamber 2, consisting of a hollow iron cylinder F, into which mercury can be run by means of a rubber tube, and an outer vessel V, which can be filled with a mixture of ice and water.
  - 4. A steam jacket 3, described in C XIII.
  - 5. A "tin" boiler with electrical attachments (C XII).

## CII. Outline of Process.

In the early part of the experiment, the chilling chamber 2 is placed directly below, and in contact with, the inner chamber of 1, U. The weighed bulb is lowered into the iron chamber F by means of the windlass, and is attached to the bottom of the chamber by the hook h. Mercury is then run in by the rubber tube t, the outer vessels, V and K, are filled with ice and water in the manner described in C IX, and the whole allowed to cool for

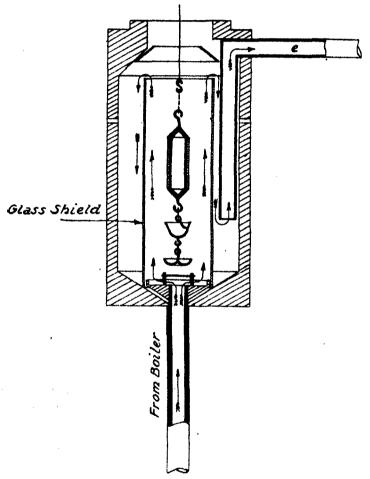


Fig. 3.-Steam Jacket.

one hour. The mercury is then syphoned off, the bulb released from h, and raised by the windlass into the inner chamber U of the vessel 1, and the slide so moved that the ice-filled depression D closes the upper chamber. The bulb is now in the insulated position described in C I (2); it is again

weighed, the ice mixture is removed from the chamber K; the chilling chamber 2 is removed, and its place taken by the steam chamber 3. The steam supply is then increased to the full; the cone C is moved so that the exit holes y, y, are free; simultaneously the outlet e (fig. 3) is blocked, and the slide is moved so that the upper chamber U is connected with the steam chamber 3 by means of the hole H. While the bulb and pan are being lowered into 3, the steam mounts into U, the supply is adjusted to the predetermined amount, the outlet e is freed, and the exit holes, y y, are closed. The consequent condensation is that due to the definite temperature change from the ice point to the boiling point under those particular conditions, and its amount may be determined by weighing the bulb in the manner described in C XIII, while it is still suspended in the steam.

#### C III. The Bulb.

The glass bulb of 8 to 10 c.e. capacity contains water and some platinum foil, so arranged that convection can take place freely. On account of the poor conductivity of the glass, the surface of the bulb rapidly approaches the temperature of the steam, and the water which condenses on its surface attains the boiling point before it reaches the glass pan P. Consequently, the condensation on the lower side of the pan itself is small (two drops), and is collected in the little glass tray T. This tray is constructed in the shape shown, so that the one large drop that collects on its lower surface can be held there securely.

#### C IV. The Filling of the Bulb.

The condensation m' is determined with the bulb nearly filled with water, the condensation m with a little water left in, so as to ensure that the interior is saturated with vapour at the higher temperature. Between these operations the bulb is opened by touching one of its fine convoluted ends on a grinding wheel, is filled with distilled water freshly boiled in a platinum vessel, and closed with a thin blow-pipe flame. By this means (1) the average temperature of the air within the tube at the time of sealing is known to within some five degrees; (2) the loss of glass is reduced to between one and three tenths of a milligramme—the thermal capacity of this lost glass is negligible, but these tenths of a milligramme must be obtained by weighing before and after the operation, and subtracted from the apparent weight of water added.

#### C V. The Joly Coil and Disc.

When the steam passes through the upper chamber 1, there is a tendency for condensation to take place at the narrow exit E. This has been prevented, as in the Joly experiment, by the electrically heated coil e, which encircles the suspension wire and warms the exit disc d by radiation. This disc has a small central hole, through which the suspension wire passes; it is light, and swings with the wire until the oscillations become smaller than the diameter of the hole; the disc then becomes steady, and the wire hangs freely through the small central hole.

#### C VI. The Glass Hook.

As the coil c is kept red, a little heat is conducted down the suspension wire (silver, about 50-gauge). The glass hook g has been inserted to check and control this quantity, which is really very small. The continuous outward flow through E carries upward and away any steam that may have come in contact with the upper portion of the suspension and become slightly superheated, and prevents any consequent evaporation from the bulb.

## C VII. The Chilling Vessel (2).

To bring the glass bulb and its attachments to the ice-point, and subsequently remove it, with few or no particles adhering, it is necessary to surround it with a conducting liquid that does not wet glass. For this reason, the chilling vessel V contains an iron cylinder F (suitably insulated by the rubber and fibre packings R, R), into which mercury can be poured by means of the tube t.

The dimensions of the platinum connecting chains c, c, are arranged so that the wire hook h can hold the bulb and pans as shown in diagram (BPT), floating inverted in the heavy mercury.

#### C VIII. Adherent Meroury and Water.

Mercury is syphoned through the tube t, and surrounds the bulb with the required conducting material. During the chilling traces of water may be deposited on its surface. On syphoning off this mercury, releasing the bulb, raising it into U and closing that chamber with the slide S, the apparent weight of the bulb will be found to have increased. The increase is the mass of adherent particles of mercury and water. The mass of mercury is obtained by drying the bulb directly after the experiment, and weighing it before and after wiping off the fine globules of mercury. The mass of water

is then determined by difference. These masses need not be large, and corrections can be applied with considerable accuracy (see E V).

The alternative method of passing a stream of dried chilled air through the air-space, and so avoiding this deposition of dew, was found to vitiate the insulating properties of the upper chilling chamber U, as the temperature and humidity of the dried air could not readily be regulated.

## CIX. Circulation in the Chilling Vessel.

To ensure that the mercury in the chilling vessel, and consequently the bulb, reaches the ice point, a slow circulation is caused in the surrounding jacket. The vessel in fig. 2 (while placed directly below and touching that of fig. 1) is filled with ice, some of which is kept at the bottom by the weighted annular net bag B. Pressed down on this is the hollow fibre cylinder C. When a steady state is reached, heat enters mainly at the side of the vessel—the slightly warmed water is the heavier and sinks, and the lighter ice-cold water within the fibre cylinder rises. The warmed water percolates slowly through the ice bag B on its way to the inner side of the cylinder C, and is thus chilled effectively so long as there is ice in B. The amount of ice in S is so chosen that it all melts in the initial stages of the cooling, and S becomes filled with ice-cold water continuously replenished by means of the circulation through B. Supercooling is thus avoided.

A similar arrangement is used with the insulation chamber (fig. 1).

In an actual experiment the chilling vessel is attached directly below the insulation chamber, and it will be seen that the mercury bath in F is surrounded by (1) the ice in V and S, (2) the chilled air of the insulation chamber, (3) the rubber R and wooden handle of the hook h, (4) the rubber of the tube t. Of the heat that leaks in, the greater portion comes through R, and an estimation of its order of magnitude may be of value.

In the figure the thickness of the steel vessel F has been exaggerated for the sake of clearness: its real thickness is about 1 mm. Seeing that the conductivity of the steel is some 250 times that of the rubber or the wood and the area of contact some 20 times greater, a temperature gradient in the steel 5,000 times smaller than that in the rubber would balance the said leak. Assuming a temperature difference of even 10° C, between the two ends of the rubber, it follows that the leak would maintain in the mercury a temperature only 0.0001° higher than it would otherwise have been. As an accuracy of 0.01° corresponds to an accuracy of one ten thousandth part of the temperature interval (100° C.), it is taken that if the mercury assumes a steady temperature at all during the experiment, that temperature is the ice point.

To check this, the chilling vessel 2 has been removed from the insulating chamber 1, and set up separately; a Beckmann thermometer inserted in the mercury in F, and the mouth of F loosely packed with cotton wool. The tendency for leaks of heat is much greater in this case, but the constancy of the temperature attained is clearly shown. Two sets of readings are given, as typical of a dozen such experiments. For the sake of comparison one set of readings is given for an experiment in which the fibre cylinder has been removed.

The magnitude of these Beckmann degrees is approximately that of a Centigrade degree. The Beckmann zero has no direct relation to the icepoint.

Table I.

Time.	Beckmann Readings.	Time.	Beckmann Readings
***************************************	Experiments with	ribre Cyli	nder.
p.m. 8.25	Insert	p.m. 3.50	Insert
8.80	8 ·08°	8.55	8 ·060°
8.85	8 -06°	4.10	8 •040°
8.40	8 ·048° ]	4.28	3 ·080°
8.41	3 ·047°	4.28	8 021° )
3.46	R - OAGO	4.80	3 ·021°
8.49	8 046° Steady	4.85	8 ·021°
4.12	5'046'   1 hamm	4.50	8 021° Steady
4.19	8 ·049°   1 nour.	5.15	8 020° period
4.80	8 '048°	5.27	8 020° 2 hours
4.35*	8·047° # )	5.50	8 ·020° 44 mins
4.46	8 ·058°	6.85	8 ·020°
4.56	8 '059°	7.12	3 ·021° }
5.4	8 ·056°	7.80	8 ·082°
5.27	8 ·075°	8.5	3 .060°
5.87	8 ·091°	9.22	3 ·123°
5.42	8 '080°	9.50	8 ·178°
5.50	8 · 089°	11.20	8 ·661°
7.2	3 ·149°		,
	Experiments witho	ut Fibre Cy	linder.
8.m.	1	p.m.	1 1
11.80	Insert	12.43	3 ·062°
11.89	8 ·17°	12.48	8 '068'
11.52	8 ·07°	1.19	8 -080°
11.56	8 '060°	1.24	3 ·22°
p.m.	. !!		oughly •
12.6	3 '0 <b>56</b> °	1.25	3.08°
12.22 12.85	8 ·056° 8 ·052°	1.26	8 ·060°

<sup>•</sup> Temperature of water outside fibre cylinder is now 1 5° C.

## C X. The Manipulation of the Insulation Chamber.

The upper chamber U is used, firstly as part of the chilling chamber, then, on closing the slot, as an insulation chamber in which the chilled bulb remains at the ice point, and, subsequently, on again opening the slot, as part of the steam chamber.

During the first stage the slot is open, and the bulb lies in the lower chilling chamber. The space K is filled with ice bags, placed round a fibre cylinder in a manner similar to that described in CIX.

During the second stage, the bulb is raised and the slot shut, giving the condition of insulation described in C I. The bulb remains here while the lower chilling chamber is being replaced by the steam chamber. When this is attached, and before the slot is opened again, i.e. while the ice in the tray D is still slowly melting, the ice bags in K are removed, the water run off, and the watertight conical cover, yy, rotated so that its three large circular holes come opposite the three large circular holes in the top of the chamber U. The slot is then opened, the Joly coil switched on, and the bulb lowered rapidly into the steam chamber. As the slot is being opened, the exit e of the steam chamber is corked, so that the steam can be made to rush into the upper chamber; subsequently e is opened, yy closed, and the flow of steam regulated to the pre-arranged amount.

As the steam rushes into the cold chamber U, driving the air before it, a belt of fog is formed at the surface of contact of the cold air and steam. This belt is set whirling and rapidly ejected, some portion of it becoming attached to the sides of the vessel and to the bulb. This is the most serious difficulty that has been encountered, and probably determines the limit of accuracy of the method. (For discussion, see E VIII, Accuracy.)

In this third stage, a stream of water is continually trickling down the sides of the chamber U, and though its magnitude is lessened by covering K with a wooden lid, great care must be taken to conduct the stream smoothly over the junction of the upper and lower chambers in order to prevent splashing.

#### · CXI. The Slide and Slot.

After considerable experimenting, it was found that a suitable slide and slot could be made out of a block of pine wood, dried for some 70 hours, and subsequently enamelled, a steam-tight fit being secured by covering the sides with strips of soft stretched felt. The difficulties are due to the facts that

\* Care is taken that the insulation vessel U is surrounded with either freezing material or poor thermal conductors. For this reason, the annular crack MM has been made in the continuity of the metal vessel.

the slide is subjected to considerable temperature gradients, is exposed to steam, and moves in a slot that expands as the temperature rises. The slot must be dried carefully after each experiment, and frequently scraped, baked, and re-enamelled.

#### C XII. The Production of the Steam.

The steam is generated electrically, a bare euroka wire immersed in water being heated by an alternating current of 40 volts and about 8 ampères.

The advantages of this method are:-

- (1) Quick response due to the small thermal capacity of the wire—the steam flow changes immediately the current is altered.
- (2) Accurate adjustment of flow—a change in the electric current produces a proportionately smaller change in the upward pressure due to the steam flow. This permits of very accurate reproduction of the steam flow, the importance of which lies in the fact that, when this pressure can be reproduced, its magnitude is of no importance in determining the difference m'-m of the two weighings in the steam chamber.
- (3) The surface of the vessel cannot rise in temperature above the boiling point, as its only source of heat is the steam and water within.
  - (4) There is no electrolysis, as the current is alternating.
- (5) By shielding the boiler and exit tubes from draughts, the degree of dampness of the steam seems to have been controlled (E VII), and its actual value seems to have been small (E IX).

#### C XIII. The Steam Chamber and Radiator Correction.

The steam chamber used by Joly was a double-walled copper vessel, the inner surfaces of which were "clean but not bright." By this means he found that a body immersed in the steam increased in weight after the initial condensation at the rate of "1 milligramme in 10 minutes." It has been found that a silvered vacuum flask reduced this to 1 milligramme in 20 minutes. The increase is due to radiation through the steam from the body at boiling point to the inner surface of the copper slightly below boiling point. It seemed, therefore, that the radiation would be checked by a glass cylinder placed as indicated in diagram 3. The outer surface of the glass will tend to become slightly chilled by radiation to the inner surface of the copper. This tendency will be counteracted by an immediate condensation of steam on the slightly chilled surface, and as the glass is a good insulator, no appreciable amount of heat can leak from the inner to the outer surface of the glass, especially as the temperature gradient is so small. Consequently the inner surface of the glass is kept very exactly at the temperature of

boiling, and loss of heat to it from the bulb is inhibited. A body immersed in a steam jacket of this kind will retain a steady weight for periods as long as 20 or 40 minutes, as is shown by the figures of Table II. Such steady readings during this long period of balance (see E VII) enable values to be obtained for m and m' under corresponding conditions without any time correction, and with the balance-arm swinging under just those steady conditions that are favourable to the accurate determination of a weight.

Table II.			
Time.		Time.	·
8.2.15		4.2.15—	
11.56 в.т.	Bulb lowered	1.4 p.m.	Bulb lowered
12 0 noon	29 ·290 grm.	1.10	35 237 grm.
12.2.0 p.m.	00.0000	1.15 "	25.0004
12.3.30	00.0010	1.18	05.0000
10 5 0 "	99 2918	1.20 ,,	85 ·2887 ,,
12.6.20 ,,	20.42017	1.07	95 .0000
12.7.30 ,	90 -9017	1.90	95.0000
12.8.30	90.9018	1,2;,	00 2009 ,, J
12.11.0	29 2916 "	23.2.15—	
12.16.30 .,	on .0010	2.12 p.m.	Bulb lowered
10.00	29 2916 ,,	2.17	29 '8890 grm.
19.95 ()	90.49010	4 30	90 -8090
10.070	90,4009	9 99 "	20,00000
10.9000	1000.00	0.05	00.40000
12.30.0 ,,	29 ·2887	13 (34)	90.40000 " >
12.01.0	ar ann ,	0.05	00.0000
10.7.15 —		0.40	00.00#1
2.86 p.m.	Balb lowered	0.10	90.0001
	28 '4000 grm. )	13.00	90.0004
	100 4004	2.46 ,,	20 0094 ,,
0.40	00.4000	81.7.15	
0.51	28 4002 ., 28 4003 .,	5.52 p.m.	Bulb lowered
ORE	00.4000	0.0	33 79 grm. (approx.)
o ra	99 -40(9)	0.0	33 '7890 grm.
0.70	00.4000	0.0	29 -701# " 7
45.70	00.4000	4.43 "	00.7010
2.09 ,,	28 4002 ,,   22 4001	6.11 ,	33 7913 ,,

D.—Corrections to be Applied.

(1) Corrections due to changes occurring within the bulb. These changes consist of change of temperature, evaporation of sufficient liquid to saturate the enclosed space with vapour, and change of pressure.

Apart from the negligible expansion of the bulb, no external work is done. The heat entering the bulb is therefore equal to the change in internal energy  $\int d\mathbf{U}$ . This quantity depends on the initial and final states of the substances and is independent of all intermediate states. The quantity of heat entering can therefore be obtained as follows:—

The complete expression for the change of internal energy may be written in the customary notation

$$\int d\mathbf{U} = \int \mathbf{C}_v d\mathbf{T} + \int \mathbf{T}^2 \frac{\partial}{\partial \mathbf{T}} \left(\frac{p}{\mathbf{T}}\right)_v dv,$$

per unit of mass.

The terms  $\int T^2 \frac{\partial}{\partial T} \left(\frac{p}{T}\right)_v dv$  which may have to be dealt with here are small.

The largest is that which refers to the compression of some 4 c.c. of water vapour from 1 atmosphere to  $2\frac{1}{8}$  atmospheres, approximately, at a temperature of 100° C. Its value may be found by taking

$$(v-b) = RT/p + c/T^n$$

as the characteristic equation of the vapour.

Whence

$$\frac{\mathbf{R}\mathbf{T}^2}{p^2}\frac{\partial}{\partial\mathbf{T}}\left(\frac{p}{\mathbf{T}}\right)_{\mathbf{v}} = -nc/\mathbf{T}^{n+1} = -n\left\{(\mathbf{v}-b)p - \mathbf{R}\mathbf{T}\right\}/\mathbf{T}p,$$

therefore,

$$\mathbf{T}^{\mathbf{a}} \frac{\partial}{\partial \mathbf{T}} \left( \frac{\mathbf{p}}{\mathbf{T}} \right)_{\mathbf{v}} = -np \left\{ (\mathbf{v} - b)p - \mathbf{R}\mathbf{T} \right\} / \mathbf{R}\mathbf{T} = \frac{na \left( \mathbf{v} - b \right)}{\mathbf{v}^{\mathbf{a}}}$$

approximately, where a is a van der Waal's constant.

 $\int_{p+1}^{p=2\frac{1}{2}} \frac{\text{Atmos.}}{\partial \Gamma} \left(\frac{p}{\Gamma}\right)_v dv \text{ is therefore of the order of } na/v \text{ ergs per gramme mole-}$ 

cule of vapour. This amount is insignificant.

The change of internal energy is therefore given to the required degree of accuracy as

$$\int d\mathbf{U} = \int \mathbf{C}_v d\mathbf{T}.$$

To obtain the corrections due to changes taking place within the bulb, consider:—

(a) M grammes of liquid and  $\mu$  grammes of air heated separately

$$\int d\mathbf{U} = \mathbf{M} \int_{\substack{0^{\circ} \text{ C.} \\ 1 \text{ iquid}}}^{100^{\circ} \text{ C.}} d\mathbf{T} - \mathbf{M} \int_{\substack{0^{\circ} \text{ C.} \\ 1 \text{ iquid}}}^{100^{\circ} \text{ C.}} d\mathbf{r} + \mu \int_{\substack{0^{\circ} \text{ C.} \\ 0^{\circ} \text{ C.}}}^{100^{\circ} \text{ C.}} d\mathbf{T} - \mu \int_{\substack{0^{\circ} \text{ C.} \\ 0^{\circ} \text{ C.}}}^{100^{\circ} \text{ C.}} d\mathbf{r}$$

(b) An amount of vapour M<sub>vap</sub>, evaporated separately at 100° C.,

$$\int \! d \, \mathbf{U} \, = \, \mathbf{M}_{\rm vap.} \, \mathbf{L}_{\rm I} \, = \, \mathbf{M}_{\rm vap.} \, \{ \mathbf{L}_p \! - \! p \, (v_{\rm vap.} - v_{\rm liq.})_{100^{\circ} \, \rm C.} \},$$

where  $L_I$  is the internal latent heat and  $L_p$  the latent heat (with 1 atmosphere pressure) at 100° C.

(The change of vapour-pressure with the absolute superincumbent pressure is of the order of 10<sup>-3</sup> of this amount and negligible here.)

(c) The pressure of each changed to p' ( $2\frac{1}{3}$  atmospheres approx.), all brought together and allowed to mix. To the order of accuracy required

$$\int d\mathbf{U} = \mathbf{0}$$
.

The expression for the heat absorbed by the bulb  $\int dU$  is, therefore, the sum of the expressions on the right-hand sides of the above equations. In the case of the emptied bulb it is equal to  $mL_p$ , and in that of the filled bulb to  $m'L_p$ . Hence,

$$(m'-m) L_{\rho} = \delta M \int_{0^{\circ} C_{*}}^{100^{\circ} C_{*}} dT - \delta M \int_{0^{\circ} C_{*}}^{100^{\circ} C_{*}} - \delta \mu \int_{0^{\circ} C_{*}}^{100^{\circ} C_{*}} dT + \delta \mu \int_{0^{\circ} C_{*}}^{1$$

where  $\delta M$ ,  $\delta \mu$ , and  $\delta M_{vap}$  are all positive.

The magnitudes of the terms on the right are approximately 400, 0.004, 0.10, 0.03, 1.30, 0.12 calories respectively. Since the experimental results cannot possibly give an accuracy greater than 1 or 2 parts in 10,000, the second and probably the fourth term may be neglected.

- (II) A correction on the weight of water added to the bulb, due to the weight of air displaced by the added water. The weight of air displaced is about 1/1000th part of the weight of water added. An error of as much as 10° C. in the estimated temperature of the air in the bulb, at the moment of closing, would produce a consequent error no greater than 1 in 30,000 in the corrected weight of the water added.
- (III) A correction for the buoyancy of the condensed liquid. The measured difference (m'-m) must be increased by an amount equal to the mass of vapour displaced by the condensation excess in the case of the filled bulb.
- (IV) A correction for the condensation due to the thermal capacity of the globules of mercury that may adhere to the bulb after the mercury has been withdrawn from the chilling chamber. These are recovered at the end of each experiment, and weighed. (C VIII and E V.)
- (V) A similar correction for the condensation, due to any traces of moisture that may become attached to the bulb while it is in the chilling chamber. (C VIII and E V.)
- (VI) A correction for the change of latent heat with temperature. The boiling point has varied from 100·27° C. to 99·41° C., corresponding to a variation of some 1 in 1000 in the supposed values of the latent heat. The consequent change in the condensation is of the order of 0·2 or 0·3 mgrm., and is corrected with sufficient accuracy by subtracting (or adding) directly from the condensation.

It will be seen that the above corrections are capable of being definitely determined. Any doubt as to their magnitude does not exceed 0.03 mgrm., though the size of the correction may be as large as 2 or 3 mgrm.

(VII) Corrections for convection, due to the heated parts, upward kinetic pressure of the stream of steam, buoyancy of the bulb (apart from the water condensed), and so on, although serious obstacles to the determination of the individual weight, are of minor importance in the present case. For this particular purpose, the difference of the weights m' and m is required. The special forms of electric heater and radiation screen (C XII and C XIII) have been devised with a view to keeping these disturbing influences of the same magnitude in both sets of weighings, so that their effects cancel when the difference (m'-m) is taken. The constancy with which these conditions are maintained is discussed in E VII.

### E.—LIMITS OF ACCURACY.

## EI. The Temperature Interval.

It has been shown (C XIII) that the weight difference m'-m can be determined to about one or two parts in 10,000, *i.e.*, 0·1 mgrm. It is sufficient, therefore, to measure the temperature interval (about 100° C.) to the nearest 0·01° C.

- (a) The temperature of the steam is determined by reading the barometer and correcting for the difference of level between it and the steam chamber. To ensure that the pressure within the chamber is not appreciably greater than that outside, the size of the exit tube has been increased, so that when boiling begins no change can be observed in the level of the water in the bent glass tube fitted into the side of the boiler. Consequently, it is taken that the temperature is measurable to within about 0.005° C.
- (b) As has been described previously, the bulb is brought to the ice point by surrounding it for upwards of an hour with mercury in a steel cylinder, the outside of which is surrounded with water, kept at the ice point by means of a free and continuous circulation through a region of melting ice. As the ice does not come into direct contact with the metal, the temperature attained by the bulb cannot fall below that of the water. This avoids supercooling of the bulb and the formation of ice within the bulb. The effect of possible heat leaks has been already discussed. The actual temperature of the melting point is obtained by analysis of the water at the conclusion of each experiment (estimation of total solids, and of carbonate present). If these impurities approached a concentration sufficient to alter the melting point  $\frac{1}{1000}$ ° C., the results of the experiments were ignored. It may be

pointed out that a supercooling of even  $\frac{1}{660}$ ° C. could by its cumulative effect freeze some of the pure water in the bulb, but an estimate of the amount of heat passing from the bulb when this very slight gradient is attained shows that this amount is immeasurably small.

It is argued, therefore, that the temperature interval has been measured to the 0.01° C. required.

## E II. The Use of the Balance.

Manly\* has determined the precautions that must be taken in the accurate use of a balance. Screens have been used in accordance with his directions and an attempt has been made to measure the temperature coefficient of the balance. This was found, however, to be quite small for the instrument used, and for the temperatures of experiment did not affect the weight by 0.1 mgrm.—the accuracy aimed at.

## EIII. The Weights.

The expression for the latent heat involves only the ratio of certain weights, i.e. (m'-m): M. It is sufficient, therefore, to calibrate the weights carefully against one another. This has been done before and after the experiments, and between the two series of experiments.

#### E IV. The Weighing in Air—Degree of Dryness.

(a) Before Chilling.—As the bulb is of glass, it collects on its surface a thin film of moisture. It is necessary that this film should be constant rather than absent. A number of weighings, taken under varied conditions as opportunity offered, showed that the weight of water expelled, on heating the bulb in a steam oven for a quarter of an hour, did not vary to any considerable extent (0.0002 grm.) with the humidity of the air which has previously surrounded it. On this account, it was found best to dry the bulb in a desiccator, and then to leave it hanging in the air for about an hour before weighing. By that time a steady weight is attained, and the mass of attached moisture is believed to vary from experiment to experiment by less than 0.25 mgrm., an amount which produces a change of 0.05 mgrm. in the mass of water condensed subsequently.

This has been found true of a room in Melbourne facing north, and for the degree of humidity usually experienced there during winter. It would seem that it is not true if the vapour pressure is low, e.g., in a desiccator, or if the relative humidity is high.

(b) After Chilling.—When the bulb has been chilled in the mercury bath

<sup>\* &#</sup>x27;Phil. Trans.,' 1907.

and raised into the chilled insulation chamber, some few particles of mercury and a little moisture adhere to it. It is important that the weight in this chamber should remain steady, i.e., there should be neither deposition nor evaporation of moisture. In the earlier trial experiments a current of cold dry air was passed to check the formation of water globules on the surface of the chilled mercury. It was found, however, that this caused evaporation when the bulb was brought out of the mercury bath. Attempts to dry the air-current to the required extent only, gave better results, but the best and steadiest results were found to be given by having no current of air at all, permitting a deposit of water globules on the mercury surface, and relying on the chilling of the upper insulation chamber to reduce the vapour pressure of the air it contains to the required amount 4.58 mm. It was found that this gave weighings steady to 0.1 mgrm.

## E V. Masses of Mercury and Water adhering to the Bulb.

The difference between the weights before and after chilling gives the sum of the weights of mercury and of water. The weight of mercury alone is obtained by drying the bulb in a steam bath after the experiment and weighing before and after removing the particles of mercury. The weight of water is then obtained by difference.

Each of these adherent masses increases the condensation. On applying corrections for these, values of the mean specific heats of water and of mercury are required, and also of the heat of vaporisation of water. The sum of these corrections may amount to as much as 10 mgrm.; but the effect of an error of one unit in the value taken for the heat of vaporisation (539 say) will cause a consequent error as low as 0.02 mgrm., and an error of one-half of 1 per cent. in the value taken for the mean specific heat of mercury effects an error of about 0.01 mgrm, in the weighing—amounts which affect the result of these experiments by only 1 part in 30,000.

# E VI. Mass of Water Added to the Bulb.

The water was prepared by distillation and subsequent boiling in a platinum vessel. The bulb and attachments were dried in a desiccator before weighing, and rapidly moved to a balance, the case of which contains a vessel of calcium chloride. The weight of water added is as much as 4 grm., so that an error of one or even two tenths of a milligramme is unimportant. In this determination, the weights of air displaced by the added water must be allowed for; knowledge of the temperature to within 20° C. is sufficient.

On enclosing boiled water with a sample of air, some solution necessarily

takes place. There is not sufficient carbon dioxide present to approach saturation of the water, so that none of this gas can be boiled off at the higher temperature. The effect of the solution in the water of oxygen, nitrogen, alkalies, etc., is more complex, but of too small an amount to affect the present work.

The method of filling the bulb is discussed in C IV.

#### E VII. Determination of the Difference between the Masses of the Condensations.

The apparent weight of the bulb and its attachments in the steam-chamber is affected by the convection upward due to the Joly coil, the upward pressure of the steam, the buoyancy of the steam, and so on. For the present purpose a difference of weights (m'-m) is required, and consequently these disturbing influences are to be made constant rather than eliminated.

(a) The Joly coil heats the windlass and is itself hot. The variation in the effect of the consequent convective currents when the Joly heating current is increased by 1 ampère, is found to be 1.8 mgrm. As the heating current is adjustable to 0.02 ampère the convection currents can probably be reproduced without variation in the weight of more than some 0.03 mgrm.

In a similar way, the effect of changing the heating current in the boiler showed that the upper pressure of the steam was reproducible to 0.05 mgrm.; and violently fanning the boiler (without removing any screens) did not change the apparent weight by more than 0.6 mgrm.

It is taken, therefore, that under good experimental conditions these disturbances do not affect the apparent weight by the smallest detectable amount (0.1 mgrm.).

(b) The steadiness of the readings obtained when the bulb is in the steam chamber has been shown (C XIII) to allow of the determination of the apparent weight to 0.1 mgrm. This steadiness might be affected by dampness of the steam, radiation to sides of vessel, and conduction of heat down the suspension wire with consequent ebullition of the water condensed above the glass hook. It is not to be expected that the ideal conditions of absolutely dry steam (E IX), complete absence of radiation, etc., have been secured, although the effects of these have been lessened wherever possible. But it is claimed that the instrument has been so adjusted that these effects completely counteract one another for a very considerable period (a quarter or half an hour); and that the weighings are taken under those conditions of steady swing which are favourable to the accurate determination of a weight.

Presumably this balance is ultimately disturbed by the complete evaporation of the moisture above the glass hook, as the apparent weight always increases before the ultimate rapid decrease begins which is due to the exposure of the heating wire as the level of the water in the boiler becomes low.

(c) The difference between the apparent weights (with filled and with emptied bulb) so obtained is the required difference (m'-m) of the condensations less the weight of steam displaced by the excess of condensed water. This buoyancy correction can be applied with great accuracy.

It would seem, therefore, that each weighing should be correct to within 0.1 mgrm., and consequently the error in the difference (m'-m) between any pair of weighings should not exceed 0.2 mgrm. That this is so, and that what may be called accidental errors are not great, is shown by the tabulated results of the two series of experiments, where the divergence of any one weighing from the mean is never more than two or three tenths of a milligramme. Consequently, the mean itself may be taken as correct to 0.1 mgrm.

A considerable number of experiments yielded results which indicated that a drop had fallen on to or off the bulb. As such a drop must weigh at least 30-50 mgrm., such results are readily isolated from the closely agreeing successful experiments, and have been discarded.

#### E VIII. Condensation (Fog) in Insulation Chamber.

A fog is formed when the steam from the steam jacket 3 comes into contact with the cold air of the insulation chamber. Some of this fog will If the whole of the air in the chamber were become attached to the bulb. to be mixed with steam, some 12 mgrm, would be condensed. part of the air, however, is driven before the steam, and is expelled at the As a liberal estimate of the amount of air mixing top of the chamber. with the steam 10 per cent. can be taken, corresponding to a condensation of 1.2 mgrm. Most of this is ejected through the large holes at the top, and of that which remains the greater part will deposit on the walls of the chamber (which have a surface seven times that of the bulb). Consequently the fog deposited on the bulb itself does not exceed two or three tenths of a milligramme, and as it is merely the variation of this from experiment to experiment that affects the value of (m'-m), no appreciable error will be introduced by this formation of fog.

#### E IX. Dryness of the Steam.

As has been pointed out in CXIII the weighings m and m' remain constant for a very considerable time and their constancy is not affected by traces of liquid damp that may be carried bodily in the steam. It is certain, however, that every particle of damp in the litre or so of steam condensed will add unduly to the weight (m'-m).

For this reason Callendar has preferred to neglect the values obtained by direct experiment, and adopts a higher value derived from the total heat formula and the specific heat of steam.

The question of dampness has been investigated in considerable detail by Richards and Mathews,\* and by the author, who believes that its effect has been reduced to insignificant proportions.

Various precautions have been taken, such as (1) slow boiling, (2) wide tubes, (3) no traps, (4) screens and jackets to avoid draughts, (5) the radius of the rubber connecting tube about the size that gives maximum lagging,† etc., so as to reduce the degree of dampness. To actually test the effect of the damp remaining, it was intended to measure the apparent latent heats under different conditions of steam supply, and from these obtain an extrapolated value for dry steam. In the second series the electric current in the boiler was adjusted so that the steam flow was some 50 per cent. greater than in the first series—the steam was given off in a much larger number of smaller bubbles—and consequently it was considered that the degree of dampness, if at all appreciable, would have been considerably affected. Somewhat unexpectedly, the values obtained (538-86 and 538-89 mean calories) were found to be identical within the limits of accuracy of the weighings.

This agreement to within three units in the fifth figure is, of course, fortuitous. Each value, however, is the result of a number of separate measurements which are consistent among themselves; each may be expected to give, and has been found to give (see Tables), a value of the apparent latent heat correct to some one part in 7000.

It has been concluded on this account that the fourth figure above is correct in each case, and consequently that the dampness of the steam has not affected the fourth figure of the result. Hence, the value of the latent heat of dry steam has been taken as 538.88 mean calories.

<sup>\* &#</sup>x27;Proc. Am. Acad.,' 1911.

<sup>+</sup> Porter, 'Phil. Mag.,' 1906.

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	Weight (corrected) of bulb, etc., in air Weight after chilling, etc. Weight adhering mercury (recovered) Weight adhering water Sum of corrections for adhering mercury	Weight of bulb, etc., in steam after condensation  Apparent weight of steam condensed  Corrected weight of steam condensed  Boiling point  Hence, apparent weight of condensation	Correction for change in latent heat with temperature of boiling Hence, corrected apparent weight of condensation per 100° C. temperature interval	Weight of bulb, etc., empty 6 5507 Weight of bulb, etc., filled 10 3829 Apparent weight of water added 3 5822 Correction for air displaced 0 0 0038 So, real weight of water added 3 58380

Second Series.

		(	-L	Tara mari		Date icari, ran (ence experiments).
weight (corrected) of bulb, etc., in air	grm. 28 90010	grm. 28 -00113	grm. 28-00006	grm. 31 :96441	grm. 31 -96993	grm. 31 -96415
Weight after chilling, etc.	28 -07320	28 -23117	28 31020	32 -32171	31 -99897	31 97324
Weight adhering water	0.01480	0.01374	0.0001	0.3131	0.0114	0.0040
Sum of corrections for adhering mercury and adhering water		0.00380	0.00370	0.01011	69700-0	0.00095
Weight of build, etc., in steam after condensation Amerent weight of steam condensed	28 52414	0.45190	28 76241	33 50840	33 18225	33 15114
Corrected weight of steam condensed	0.44784	0.44810	0.44851	1.17658	1 .17859	1.17695
Boiling noint		ပ် နို ဇ	° C.	့ ၁.၅	့ ၁ ခု	° C.
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Hence, apparent weight of condensation per 100° C. temperature interral		0.44837	0.44838	1.17998	1.18036	1 18035
Correction for change in latent heat with change of temperature	perature 0.00007	0 .00003	0 -00002	0 -00038	0.00019	98000.0
of botting Hence corrected apparent weight of condensation per 100° C.	100° C. 0.44868	0.44840	0.44836	1.18036	1.18055	1.18073
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Weight of bulb, etc., empty 6 66111 Weight of bulb, etc., filled 10 61663  Apparent weight of water added 3 95552 Correction for air displaced 0.00396 So, real weight of water added 3 856948	Mean apparent condensation with filled bulb  Apparent value of difference Corrections for changes occurring within the bulb Correction for difference of buoyancy of amounts of water condensed Weight of water M added to the bulb Weight of water M added to the bulb Whence, the heat of vaporisation of water boiling at 100° C, and at P atmosphere	ation with filled action with complete for contraring within the cof buryancy of condensatic ded to the bulb.	bulb ied bulb in the bulb f amounts of ins, m'-m, per	water condense 100° C. tempe at 100° C. and	dd mature interra at b atmosph	grm. 1 18655 0 14845 0 073210 0 00025 0 00025 0 073479 1 0 73479

#### F. Conclusion.

Determination with first bulb, 538.89 mean calories.

Determination with second bulb, 538.86 mean calories.

These determinations are independent in the sense that they have been made with different bulbs and under different conditions of steam supply, and that any one measurement is used in one series only.

The values may be expected (see E) to agree to within seven or eight units in the fifth figure, a degree of accuracy that is confirmed by the experimental figures (see Tables).

The conclusion is therefore that the value

#### 538.88 mean calories

for the heat of vaporisation of water at 100° C. and 1 atmosphere pressure is correct to the fourth significant figure for the samples of steam used; and in consideration of the results of Section E IX, it is held that the dampness of these samples has not affected the result to the extent of 1 part in 5000.

My thanks are due to Prof. Lyle(1914) and subsequently to Prof. Laby(1915) for kind advice and for placing at my disposal the facilities offered by the physical laboratories and workshop of the University of Melbourne; to Prof. Porter and Dr. Rosenhain for advice as to the method of presentation of the work; and to Mr. A. E. Dawkins, B.Sc., to whose skill and enthusiasm during several months of collaboration in the earlier part of the experimental work I am much indebted.

## The Magnetic Storm of August 22, 1916.

By C. CHREE, Sc.D., LL.D., F.R.S., Superintendent of Kew Observatory.

(Received January 31, 1917.)

§ 1. While the ultimate cause of magnetic storms has been a fruitful source of speculation, detailed enquiries into the phenomena presented by individual storms have been comparatively few. This distribution of effort is to be regretted, because, without accurate knowledge of the phenomena, theoretical investigations are apt to be barren of results. A difficulty in the way is the great complexity of the magnetic changes which take place, even at a single station, in the course of the ordinary magnetic storm. Some of these changes are undoubtedly more local and of less general significance than others, but the difficulty is to see anything but accident in the sequence of events.

Of late years an international scheme has existed for the selection of a limited number of magnetic storms annually, co-operating stations publishing copies of the magnetograms obtained on these particular days. A considerable number of records have accumulated, but few serious attempts have been made to utilise them. The most hopeful course is, I think, to start with the study of those magnetic disturbances of considerable amplitude which appear of the simplest kind.

The simplest type of disturbance one can imagine is that which would result from the gradual waxing and waning of an electric current in a fixed circuit. In such a case we should expect to see a gradual departure in each magnetic element from its undisturbed or normal value, the element passing through a maximum or minimum, and returning gradually to its undisturbed value. The changes in the several elements would be in phase, the maximum or minimum value occurring simultaneously in all.

The trace in a magnetogram in such a case would resemble fig. 1, the portions AB, DE of the trace corresponding to the normal value of the element, BD being greater or less according to the time taken by the magnetic change and the openness of the time scale. Instead of a single oscillation, we might have a double oscillation as in fig. 2, or a succession of



them. The movement in fig. 2 might arise from an electric current in a fixed circuit, whose direction reversed in passing through a zero value.

On the hypothesis mentioned, the departures at one and the same instant of time of any two magnetic elements from their normal values would stand to one another in a constant ratio, which obviously implies constancy of direction in the disturbance vector.

§ 2. Now, there are occasions when the magnetic curves show at least an approach to this state of matters. But supposing a source of disturbance equivalent to the fluctuations of an electric current in a fixed circuit to come into operation, one would hardly anticipate the total suspension during its action of other magnetic changes, such, for instance, as those which constitute the regular diurnal variation. Also the presence of any second source of magnetic change would interfere more or less with the regularity of shape of the magnetic curves, and it would naturally affect the different elements differently. The turning points might be accelerated in one element and retarded in another, so that the movements in the curves for different elements at a single station would no longer appear strictly in phase.

In the ordinary magnetogram, the length of trace per minute of time is only from  $\frac{1}{4}$  to  $\frac{1}{3}$  mm., while the dot of light producing the trace is of finite size. Thus, even under the most favourable conditions, it is difficult to fix the time of any movement to nearer than half a minute, and as the trace at a turning point has generally a finite curvature, the accuracy with which the time of reversal of a movement can be fixed is usually less than this. Thus it is usually impossible to affirm with certainty that two magnetic elements at the same station are absolutely in phase, and, conversely, the existence of a small difference of phase is apt to be rather a matter of belief than of exact demonstration.

When discussing the magnetograms obtained in 1902-4 by the National Antarctic Expedition,\* along with corresponding curves from co-operating stations, I came across some cases of simultaneous, or nearly simultaneous, short movements in the traces from different stations. These movements were generally oscillatory, i.e., the element tended to return towards the original undisturbed value. But the to-and-fro movements were seldom, if ever, absolutely equal, and I preferred to regard them as separate movements distinguished by the letters A and B. At a particular station the A movements had a more or less common direction, and so had the B, and the average directions for the two types were not far from being opposite to one another. In such a case, as suggested above, the departure

<sup>\* &#</sup>x27;National Antarctic Expedition, 1901-4, Magnetic Observations,' pp. 176 et seq.

from direct opposition in the to-and-fro movements may arise from the action of an independent source of disturbance. If so, our best course would probably be to treat the two movements as the two halves of an oscillation due to a simple source, as we might reasonably hope in this way to eliminate in considerable measure the effects of the second source of disturbance. But, on the other hand, the departure from exact opposition between the two movements may be an essential, not an accidental, feature, and if so, the conception of a to-and-fro oscillation in a given azimuth may be the reverse of helpful.

In dealing with the Eskdalemuir curves for 1913 and 1914, Mr. L. F. Richardson\* came across a number of cases which he believed to represent oscillation in a fixed azimuth. These he called disturbances of class K. In other disturbances, which he called class L, he found the movements in the different elements to differ in phase.

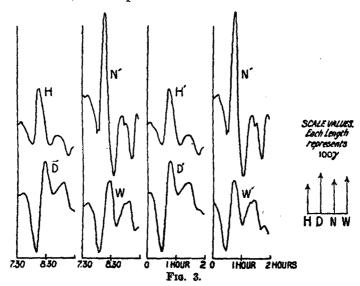
Personally, I am inclined to think that it is at least highly exceptional for the movements in the different elements to remain absolutely in phase for any appreciable length of time. However this may be, there can be no doubt that differences in phase between the different elements are much more in evidence in some cases than others. When there is a difference of phase between the two components in, say, the horizontal plane, the azimuth of the disturbance vector in that plane continually alters. The fact that the vector diagram often represents a rotation which proceeds in one direction for a considerable time, it may be hours, the rotation being either clockwise or counter-clockwise, was first pointed out by Mr. R. B. Sangster. Dealing with the copies of disturbed curves, published annually at Greenwich, he found no less than 70 examples of the phenomenon. Analysing them, he found the direction of rotation to be largely dependent on the hour of the He observed no single instance of what he called a "positive" (or clockwise) rotation between 4 P.M. and 9 P.M., while in the early morning this direction was the more common one.

- § 3. The disturbance I am now about to describe is one in which the rotation in the disturbance vector diagram is so remarkably pronounced and regular as to invite special study. It began with a "sudden commencement," especially prominent as usual in the horizontal force, at about 6 h. 30 m. r.m. on August 22, 1916, and continued until the morning of the
- \* Meteorological Office, 'British Meteorological and Magnetic Year Book,' Part IV, Section 2, p. 78, 1913.
- † 'Roy. Soc. Proc.,' A, vol. 84, p. 85. Note.—Mr. Sangster really considered the vector diagram in the plane normal to the dipping needle. But the directions of rotation seen in it and in the horizontal plane are usually the same. The latter depend only on variations of the horizontal components, which are usually the most reliable.

23rd. As usual, the curves did not become really quiet for a considerable time, but no large movements took place after 5 a.m. on the 23rd, and at Kew Observatory the specially conspicuous movements took place between 7 p.m. and 11 p.m. on the 22rd. Attention is restricted here to these hours, and more especially to the interval 7.48 p.m. to 9.24 p.m. A display of aurora on the evening of the 22rd was reported from one Scottish meteorological station—Stornoway—but it does not seem to have been in any way outstanding. The duration of twilight, however, at that season would naturally interfere with the visibility of aurora in Scotland during the earlier part of the magnetic storm.

The artificial disturbances from which the Kew magnetic curves now suffer render them unsuitable for the study of minor details of most natural disturbances, but, on August 22, 1916, the natural disturbance was so large that the uncertainties connected with the measurement of the H and D (horizontal force and declination) traces were not serious. Vertical force (V) measurements at Kew are exposed to much more uncertainty. Photographic copies of the Eskdalemuir curves were kindly supplied by Dr. Crichton Mitchell, Superintendent of the Observatory. The horizontal components recorded at Eskdalemuir are not, as usual, H and D, but N and W, the north and west components. This stands somewhat in the way of optical intercomparison of the curves at the two observatories.

In fig. 3 H and D are copies, reduced to half, of the Kew horizontal force and declination traces from 7.30 P.M. to 9.30 P.M. on August 22, set to a common time scale, so that points on the same ordinate refer to the same



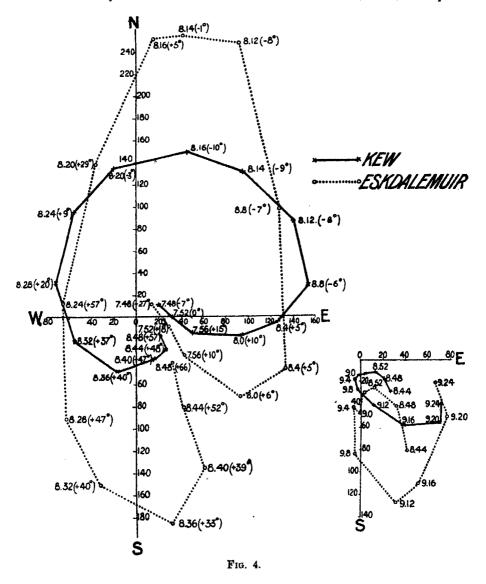
instant of time. N and W are the Eskdalemuir north and west component traces, similarly set and reduced, for the same interval. The time scales at the two observatories are closely alike, one hour being represented by about 15.3 mm. The ordinates' scale values were as follows: 1 mm. equals  $6.1 \gamma$  in H,  $4.6 \gamma$  (or 0.87') in D,  $5.0 \gamma$  in N, and  $5.3 \gamma$  in W. H' and D' are identical with H and D, only D' has been moved to the left relatively to H' by the equivalent of 10 minutes of time. In other words, if t be the time in minutes to which a point on a given ordinate in the D' curve answers, the point on the same ordinate in the H' curve answers to the time t-10. Similarly, N' and W' are the same as N and W, but for a relative displacement corresponding to about 10 minutes of time.

Declination at Kew Observatory is about 15.1° W. We may thus regard the H and D curves as showing the changes of force in two rectangular directions, the first inclined 15:1° west of north, the other 15:1° south of west. Again, while the H and D curves in fig. 3 are not in phase, the difference in phase is not large, and there is a considerable resemblance between the curves. Hence, if N and W component magnetographs had been in operation at Kew, the resemblance between the N curve and the H curve and between the W curve and the D curve would have been pretty close. It follows that the variation in the N component at Eskdalemuir was very much larger than the corresponding variation at Kew. Eskdalemuir is not very far from the English border, the difference between the North of Scotland and the South of England may well have been twice as great as between Eskdalemuir and Kew. To arrive at an adequate conception of the variations of magnetic force during a disturbance of this type, even in such a limited area as the British Isles, obviously requires the co-operation of at least four or five well distributed stations.

It is obvious at a glance that D is not in phase with H, nor W with N. It is equally clear that, if no time difference had existed between D' and H', and between W' and N', we should have regarded either pair of curves as showing a close approach to identity of phase throughout the greater part of two hours. At the same time, the ratio of the amplitudes of the successive oscillations is not the same for the two elements, so that, even if the records had been simultaneous, the azimuth of the disturbance vector would have undergone change.

§ 4. To study details, the curves were measured at 4-minute (or very nearly 1 mm.) intervals, and, to facilite comparison, the changes in H and D at Kew were converted into changes in N and W. The values of the elements immediately before the sudden commencement at 6.30 r.m. were accepted as normal, and it is the differences from these normal values,  $\Delta N$ ,

 $\Delta$ W, and  $\Delta$ V, that appear in Table I. The inclination to the horizon  $\psi$  of the vector, whose rectangular components are  $\Delta$ N,  $\Delta$ W, and  $-\Delta$ V, was calculated only for the interval 7.48 P.M. to 9.24 P.M., to which special



interest attaches, and the values of  $\Delta V$  at Kew are confined to the same interval. A + sign in  $\psi$  means inclination above the horizon. The extreme values of  $\Delta N$ ,  $\Delta W$ , and  $\Delta V$  are distinguished by heavy type. A fair idea of the relative size of the disturbance at the two stations is

Table I.—Departures from the "Normal" Values.

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derivable from the ranges\* of the elements, as shown in the Table, viz., at Kew  $\Delta N = 211 \gamma$ ,  $\Delta W = 226 \gamma$ ,  $\Delta V = 80 \gamma$ , and at Eskdalemuir  $\Delta N = 441 \gamma$ ,  $\Delta W = 199 \gamma$ ,  $\Delta V = 179 \gamma$ .

The range in W is slightly larger at Kew, but the Kew ranges in N and V are barely half those at Eskdalemuir. Ranges as large as  $600\,\gamma$  in magnetic storms have been recorded, though very rarely, at Kew, but a range of 441  $\gamma$  in the course of 22 minutes, as presented by the N trace at Eskdalemuir, would be very notable, if not absolutely unprecedented, in any element at Kew.

The extreme steepness of the curves, especially the Eskdalemuir N curve, rendered the measurements more difficult, and the results less certain than usual, because a very small error in the time, or a very small tilt in the measuring scale, would have unusually large effects.

Exception may be taken to the normal values accepted. This is generally a difficulty. Perhaps the most approved plan is to accept as the normal value at any hour the arithmetic mean of the values at that hour on all the quieter days of the month or a selection of them. The object is to eliminate the regular diurnal variation, the contribution from which varies from hour to hour. This method is, however, not so satisfactory as it was once supposed to be, because we now know that the amplitude and character of the regular diurnal variation are considerably affected by the presence of disturbance. Also the strict application of this method to a case where measurements are taken at intervals not of one hour but of four minutes would entail so much labour as to be justifiable only if one felt assured of its marked superiority. In favour of the course adopted, it may be urged that the Kew curves at least were practically quiet up to the time of the "sudden commencement," and that the ordinary diurnal variation during the evening hours covered by the Table is so small compared with the changes which actually occurred that it is practically immaterial how we treat it.

§ 5. The results in the horizontal plane between 7.48 P.M. and 9.24 P.M. are shown as vector diagrams in fig. 4. To prevent confusion the intervals 7.48 P.M. to 8.48 P.M. and 8.44 P.M. to 9.24 P.M. are illustrated by separate diagrams, with distinct origins and axes of co-ordinates. The overlap of four minutes is intended to assist the eye in passing from consideration of the one interval to the other. The full line curves with observational points indicated by crosses refer to Kew, the dotted curves with observational points indicated by circles refer to Eskdalemuir. Unity in the forces marked on the co-ordinate axes represents 1  $\gamma$ . The times to which the observational points

<sup>\*</sup> The ranges as shown on the Kew curves are  $\Delta H = 225 \gamma$ ,  $\Delta D = 42'$ .

refer are shown, and alongside from 7.48 P.M. to 8.48 P.M. are the corresponding values of the inclination  $\psi$ .

A thing to be noticed is that the length and direction of the vector drawn from the origin to any observational point are dependent on the values accepted as normals for N and W, and so are to some extent arbitrary. If, however, we treat the normals as constants, a change in the values accepted has no influence on the shape of the curve obtained by connecting up the observational points, or on the direction in which it is described by a point travelling continuously along it. A change in the normal values accepted is really equivalent to a transfer of the origin of co-ordinates from one point to another. If, for instance, we had taken normal values for N larger by  $60 \gamma$ , and for W larger by  $40 \gamma$ , we should have had an origin nearly central for both the diagrams relating to the interval 7.48 p.m. to 8.48 p.m.

The diagrams are obviously described counter-clockwise throughout, and so in the direction which Mr. Sangster found to be characteristic of the evening hours at Greenwich. The outstanding feature is the regularity of outline in the diagrams for the interval 7.48 p.m. to 8.48 p.m.

If corresponding points are joined in the Eskdalemuir and Kew diagrams, it will be found that in most cases the connecting line is oriented roughly N.N.W. (or S.S.E.). Departures from this direction are seldom marked, unless the two corresponding points lie close together, when a small error in the time or in the curve measurement for either station would exert an unusually large influence on the azimuth. This suggests that the disturbance field at Eskdalemuir might be obtained by superposing on the disturbance field at Kew a field the vector in which shows but small departures from a fixed direction, this direction being roughly that of the line connecting the two stations.

§ 6. The magnetic changes constituting the regular diurnal inequality are almost certainly due in the main to electrical currents in the upper atmosphere. These changes show a clear dependence on local time, and so are presumably ultimately due to the sun. The solar influence may be purely electrical, e.g., a flight of electrons, or largely thermal. If it is thermal, the difference between the diurnal variations on quiet and disturbed days, and between the diurnal variations in years of many and of few sunspots, seems to prove that the strength of the currents is not determined solely by the intensity of the thermal action, but partly by other causes. The most natural hypothesis is that these other causes reduce the electrical resistance of the upper atmosphere and so increase the magnitude of the currents to which the diurnal variation is due. The facts that the character of the diurnal inequality shows a marked dependence on the latitude, and that the phase is determined by local time.

suggest that electrical currents are present throughout the whole of the upper atmosphere, and that the phenomena are chiefly dependent on the current existing within a moderate distance of the zenith of the place.

The influence of local time is also recognisable in the case of magnetic disturbance. For instance, the main features of the phenomena presented by the vertical force at Kew during a magnetic storm can generally be foretold by reference to the hour of the day. But large magnetic disturbance in Britain is usually accompanied by aurora, as was the case on August 22, and aurora, at least in England, is usually comparatively low down towards the northern horizon. Of course, the electrical discharges causing aurora may not be confined to the regions of the sky where aurora is visible. Below a certain intensity they may be invisible and, if so, the disturbance at a station in low or mean latitudes may be mainly due to invisible currents near the zenith, and only in a minor degree to currents existing where aurora is seen.

The fact that the disturbance of August 22 was much larger at Eskdalemuir than at Kew might mean that the disturbance at both places was mainly due to electrical currents restricted to a limited area, considerably nearer to Eskdalemuir than to Kew, or it might mean that electrical currents present in all latitudes were much stronger in the latitude of Eskdalemuir than in that of Kew.

Aurora is much more in evidence in Scotland, especially the North of Scotland, than in the South of England; thus, if the disturbing currents are limited to the regions of the atmosphere where aurora is visible, they would in the ordinary course be some 300 miles nearer to Eskdalemuir than to Kew. The magnetic force due to a very long straight current varies inversely as the distance from the current, while the strength of the field due to a closed electrical circuit at a distance large compared with the largest diameter of the circuit varies as the inverse cube of the distance. Thus, if the disturbance of August 22 were due to currents restricted to a definite limited portion of the atmosphere we must suppose that portion of atmosphere to have been a few hundred miles north of Eskdalemuir. It is, however, difficult to imagine how electrical currents situated a few hundred miles north of Eskdalemuir could produce the changes of field exhibited in fig. 4. A change in the sign of W would naturally arise if the nearer portions of current were oriented east-west, and the centre of the current area moved across the meridian of the station, and would thus naturally present itself nearly at the same time at Eskdalemuir and Kew, as was indeed the case. But we should expect the range of W to be greater at the nearer station, while the reverse occurred. If a current of given sign continued to flow in a straight horizontal circuit, a change would naturally

occur in the sign of  $\Delta V$  when the circuit crossed the zenith of the place. But such transit would not change the direction of the horizontal component of force. It will be seen, on consulting Table I, that  $\Delta V$ , while generally negative, was distinctly positive for a short time, a little after 8 p.m. at both stations. The change from — to + in  $\Delta V$  occurred nearly, if not quite, simultaneously with a corresponding change of sign in  $\Delta N$ , though  $\Delta V$  reverted to the minus sign some minutes before  $\Delta N$  did. A change of sign from minus to plus also took place in  $\Delta W$ , but decidedly later than in the other elements. These changes of sign seem difficult to account for on the hypothesis of mere change of position in the circuit of a definite electrical current. They suggest changes in the direction of the current as well.

If the disturbance were due to electrons from the sun, these, according to Profs. Birkeland and Störmer, should describe spirals round the lines of force of the earth's magnetic field, and so should be approximately equivalent to a current following the lines of force, but not extending below the upper regions of the atmosphere. Störmer's observations and estimates—made, however, in years of sunspot minimum, when the electrons may be easier stopped—put the lower limit of aurora as usually a little less than 100 kilom. One would expect the horizontal component of force due to such a discharge to have an east-west rather than north-south azimuth, while the vertical component would naturally be small except near the margin of the area which had the discharge overhead.

In view of the many possibilities, speculations based on the phenomena seen at two stations only are unlikely to hit the mark. In cases such as the present, a third station in the North of Scotland, preferably in the Orkneys or Shetlands, would undoubtedly be more helpful than any station in central or southern Europe. It is hoped that the present paper, besides encouraging investigations at other observatories into this particular storm, may secure increased attention to the interesting phenomenon discovered by Mr. Sangster. A study of the diurnal variation in the direction of rotation of the disturbance vector in different parts of the world should lead to results of interest.

Spontaneous Generation of Heat in Recently Hardened Steel.\*

By Charles F. Brush and Sir Robert A. Hadfield, F.R.S.

(Received January 17, 1917.)

The object of this paper is to show that various kinds of steel, including carbon tool steel, "high speed" tungsten-chromium steel, and other similar iron alloys, after being quenched at a high temperature and hardened, spontaneously generate heat for at least several weeks in appreciable and measurable quantity, the rate of generation of course steadily diminishing.

The paper is divided into two sections. First the research work relating to this discovery which originated with one of us (Brush) and which in the second part has been further experimented upon and verified by one of us (Hadfield). As the paper contains important new facts of much interest, it seems desirable that the results should be brought before the Royal Society.

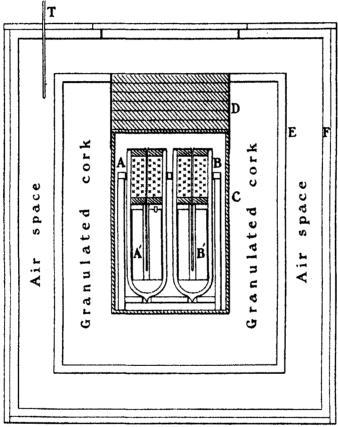
Fig. 1 is a diagram of the apparatus employed. A and B represent two large silvered Dewar vacuum jars selected to have very nearly equal thermal insulating efficiency. They are supported in a wooden rack inside a thick copper cylinder C, packed in granulated cork in a wooden box E. D is a paper extension of C, packed with layers of felt, by removal of which and the loose copper cover of C, easy access is had to the Dewar jars. The copper cylinder weighs 52 lb. and its functions are, by reason of its large thermal capacity and high conductivity, to protect the Dewar jars from any rapid change of temperature, and from temperature stratification.

The box E is surrounded by a much larger wooden box F, lagged with felt. By means of a long resistance wire and thermostat, not shown, the air space between the boxes may be maintained at constant temperature.

A' is an air-tight cylinder of thin copper, 6 inches high and  $2\frac{1}{2}$  inches in diameter, provided with an open half-inch axial tube, also of copper. A small round opening at the top of A' permits the introduction of a weighed quantity of water, after which the opening is tightly corked to prevent any change of temperature by evaporation of the water. B' is another copper cylinder just like A', except that it has a removable top to permit the introduction of the substance whose thermal behaviour is to be investigated. The high thermal conductivity of these copper cylinders prevents temperature stratification within them. The Dewar jars are filled above the copper cylinders with layers of felt and granulated cork, and covered with waxed

<sup>\*</sup> Brush, in April, 1915, presented a paper to the American Philosophical Society with regard to this subject. 'Proc. Amer. Phil. Soc.,' vol. 54, No. 217 (May-July, 1915).

cardboard carefully sealed on to prevent temperature-difference inside the jars which would follow unequal loss or gain of moisture by the felt and granulated cork. A small thin glass tube, flanged at top and closed at bottom, is located in the axis of each Dewar jar and extends from the waxed cover nearly to the bottom of the enclosed copper cylinder. The glass tubes contain the ends of thermo-electric couples of fine constantan, copper and iron wires, one iron-constantan and one copper-constantan junction at the



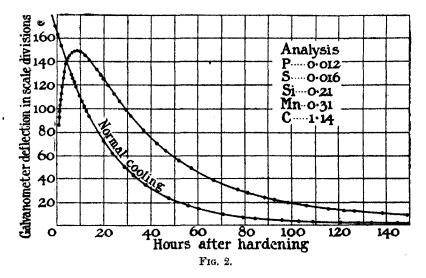
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bottom of each tube. The leading-out wires are copper, and connect the thermo-couples with a reflecting galvanometer having the customary reading telescope and scale. Careful calibration has shown that 55 scale divisions of the galvanometer indicate 1° C. temperature-difference between A' and B', and that temperature-difference and galvanometer deflection are very closely proportional throughout the range used.

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In the following experiment A' and B' were removed from the Dewar jars and allowed to attain equal room temperature. Twelve half-inch round bars of tool steel, 5 inches long and with machined surfaces, were hardened by heating to high "cherry-red" in a reducing atmosphere of a gas furnace and quenching in cold water. The bars then had a thin and strongly adhering coating of black oxide. They were next stirred in a large quantity of water at room temperature, to acquire that temperature, wiped dry, and oiled with heavy, neutral mineral oil to prevent generation of heat by further surface oxidation, wiped free of excess of oil and placed in the copper cylinder B'. A weighed quantity of water, also at room temperature, just sufficient to equal the steel bars in thermal capacity had already been placed in A'. The whole apparatus was then assembled as quickly as possible, and galvanometer readings commenced.

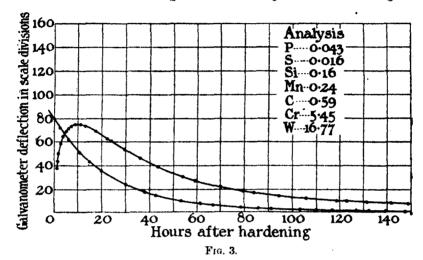
The upper curve in fig. 2 shows the progress of heat generation in the carbon tool steel bars during the first 150 hours after hardening.



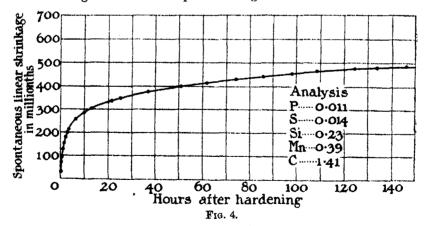
The "normal cooling" curve was obtained five or six weeks after the other, and when the generation of heat had very nearly ceased. For this purpose the steel bars were removed, warmed a few degrees, and replaced; then galvanometer readings were made from time to time as before. This curve is plotted in a location convenient for visual comparison with the heating curve, but otherwise might just as well be plotted farther to the right. For studying the generation of heat at any point in the upper curve, the curve of normal cooling may be plotted where it will intersect the upper curve at the desired point.

The tungsten-chromium steel, consisting of the same number of bars of the same dimensions as in the first experiment, was treated in the same manner.

Fig. 3 shows the curve of heat generation in the tungsten-chromium steel, and the curve of normal cooling located with respect thereto, as in fig. 2.



Further experiments show that carbon steel, when hardened, remains very considerably expanded, and that it shrinks progressively when "tempered" to various stages, and finally annealed. A long thin bar of high carbon steel was found to shrink spontaneously after hardening, to such an extent that its progress was easily measured and followed for many days. The spontaneous shrinkage of this steel is plotted in fig. 4.



It was further shown that while spontaneous generation of heat was probably accompanied by spontaneous shrinking in the specimen of steel examined, yet the shrinking could not possibly be the prime cause of the heat, because the work represented by the heat generated was hundreds of times more than sufficient to effect the reduction in volume that probably occurred. This conclusion, that shrinking was not the cause of the generation of heat, has been questioned; but the more recent experiments, some of which show no shrinking during the generation of heat, confirm it.

One of us (Hadfield) prepared two sets of specimens of nickel-chromium steel, of which the analyses are given in the accompanying figures, which were tested for spontaneous generation of heat after hardening. Each set of specimens consisted of twelve half-inch round bars, five inches long, with machined surfaces, so that results obtained would be quantitatively comparable with those of the other kinds of steel formerly examined.

Specimen A was gradually heated in a gas furnace, with reducing atmosphere, whilst its magnetic susceptibility was observed from time to time by means of a simple induction apparatus devised for the purpose. Susceptibility remained substantially constant until cherry-red heat was reached, then soon rose 10 per cent. or more, and again remained constant, at the higher value, for several minutes, then fell off rapidly to nothing. This was taken to indicate complete decalescence, and the proper temperature for hardening. The furnace was immediately opened, and the twelve bars quenched separately in water and crushed ice, then stirred in much water at room temperature, wiped dry, oiled, and placed in the calorimeter (fig. 1), all as in the earlier experiments first described.

Fig. 5 shows the progress of heat generation following this first hardening of specimen A of the Hadfield nickel-chromium steel. Rapid generation of heat is indicated in the early stages, especially during the first hour, and maximum temperature, the point at which gain of heat was balanced by normal cooling, was reached in about 3½ hours. Obviously the rate of generation had diminished very much by that time, and was falling fast, though it still retained considerable value at the end of 150 hours. In general, the curve of "first hardening" clearly indicates that the rate of heat generation diminished steadily from the moment of quenching the hot steel.

After a week of cooling, the same bars were again placed in the furnace and heated to a temperature considerably higher than before, by continuing the heating 15 minutes after complete loss of magnetic susceptibility. They were then quenched and treated as formerly.

The other curve of fig. 5 shows the effect of the higher quenching temperature. Generation of heat was at first much slower than before, the far lower maximum temperature requiring 8 hours to reach; but the generation was

much better sustained, as indicated also by the crossing of the curves after 35 hours. The total amount of heat generated was not greatly different in the two cases.

Specimen B of the Hadfield steel was treated in "first hardening"

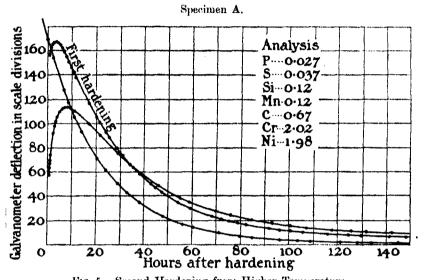


Fig. 5.—Second Hardening from Higher Temperature.

precisely like specimen A; but in second hardening was not heated quite so far above the temperature of decalescence.

Fig. 6 shows progress of heat generation in specimen B after first and

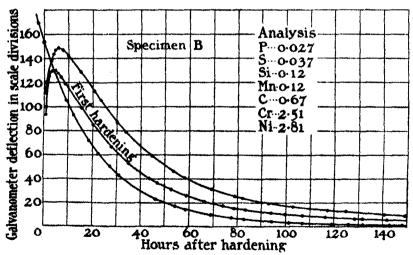


Fig. 6.—Second Quenching from Higher Temperature.

second hardening. The total amount of heat generated was much greater after the second hardening than after the first; B differed greatly from A in this respect. Probably this was due to the different carbon, chromium, and nickel content, as shown in the analyses of the two specimens.

The effect on specimen B of a moderate increase in quenching temperature was so great that it was thought worth while to quench it a third time, at a temperature somewhat *lower* than in "first hardening," and the temperature of complete recalescence was chosen; so that while the quenching temperature of first hardening was just above the critical temperature of decalescence, that of the third hardening would lie just below the critical temperature of recalescence. In this way light may be thrown on the cause of the spontaneous generation of heat.

With regard to the third quenching of specimen B, alluded to as the "third hardening," this having been quenched below the critical temperature is, of course, not hardened in the true sense, but would be slightly stiffer than material in the annealed condition.

In pursuance of this idea, specimen B was again slowly heated in the gas furnace until complete loss of magnetic susceptibility was reached. This was the quenching temperature of first hardening. Then the supply of gas and air was so far reduced that the furnace very gradually cooled. In about 20 minutes the steel commenced to regain its magnetic susceptibility, and a few minutes later had completely regained it. The bars were immediately quenched, and treated as formerly.

It was expected that the spontaneous generation of heat would be greatly modified, or possibly eliminated, by thus quenching the steel below the critical temperature, because true hardening could not have taken place. But it was not so. On the contrary, fully three-fourths as much heat was generated as followed the first hardening, and its curve (not plotted) was parallel throughout with that of "first hardening." It may, therefore, safely be concluded that the spontaneous generation of heat, at least in the case of specimen B, was not associated with the phenomenon of recalescence.\*

\* With reference to the foregoing statement, one of us (Hadfield) has since carried out tests on specimens quenched from just below the critical point. The results are shown in the diagram (fig. 14) and Table VII. It will be seen that in this case there is no measurable evolution of heat. Quenched from above the critical point as shown on diagram (fig. 9), the Brinell ball hardness number was 740, and a rise of temperature of 1.35° was measured. In the specimen now referred to there is a slight stiffening, that is, the ball hardness number of the steel has increased from 200 in its ordinary softer condition up to 300 after treatment in the above-mentioned experiment. It will be seen that no measurable evolution of heat occurs. In other words, the slight increase of hardness from 200 to 300 is due rather to the mechanical or slightly strained condition of the metal, but there is no real hardening.

It has been suggested that some, at least, of the spontaneously generated heat found in all these experiments may have been due to chemical action of residual moisture or oil, or both, on the metal or its coating of oxide. To meet this criticism, specimen B was again slowly heated until it began to lose its magnetic susceptibility. This was above the temperature of the previous quenching, and presumably obliterated its effects; it also destroyed the oil and oily compounds, if any, of the previous operation. Then the furnace was closed and, with its contents, allowed to cool 4 hours. The steel bars were then removed from the furnace, still too hot to handle, allowed to aircool half-an-hour longer, stirred in much water at room temperature, wiped dry, oiled and placed in the calorimeter just as formerly. The slow leakage of air into the hot furnace after closing had provided the steel bars with a thin coating of black oxide having the same appearance as that which followed the previous quenchings. The aim of all this procedure was to reproduce as faithfully as possible all the conditions which obtained in previous experiments, except hardening.

In all former experiments the temperature of the steel had risen considerably during the assembling of the apparatus immediately following the oiling of the bars, as shown by the curve sheets. But in this case the first galvanometer readings were slightly minus, showing that the steel was about one-fiftieth of a degree colder than the balancing water in the other Dewar jar; and several days passed before approximate equality of temperature was reached. Hence we may safely say that not the slightest trace of heat was generated in the steel, and that the heat generation observed in former experiments was surely due to hardening.

Before commencing the experiments with specimens A and B above detailed, a test bar of each lot was prepared by machining its ends slightly convex and polishing, so as to permit of accurate length measurements by means of a micrometer calliper easily manipulated to constant end-pressure, and easily read to one twenty-thousandth of an inch. The test bars were mechanically held always in the same position between the calliper jaws.

Measurements of the test bars were made after various treatments, and the results are shown in Tables I and II. The error of measurement does not exceed one unit in the last decimal.

It will be observed that in neither case was there any spontaneous shrinking after the first hardening, thus demonstrating that the heat generation which then occurred was not due to shrinking.

In both specimens total shrinkage was about twice as great after second hardening as after first hardening, but was divided between the several treatments quite differently. Thus, comparing second hardening shrinkages

Table I.—Specimen A.

	First hardening.	Second bardening.
	inches.	inches.
Length of test bar—		
After hardening	5 .0274	5 0354
After spontaneous shrinking	5 .0274	5 0842
After tempering to light straw	5 .0268	5 0298
After tempering to light blue	5 .0255	5 .0298
After annealing	5 .0222	5 .0250

Table II.—Specimen B.

	First hardening.	Second hardening
	inches.	inches.
Length of test bur—		1
After hardening	5 0180	5.0151
After spontaneous shrinking	5 .0180	5 0143
After tempering to light straw	5 .0172	5 .0093
After tempering to light blue	5 .0161	5 .0091
After annealing	5.0139	5 .0063

with first: considerable [occurred spontaneously (none in first); about five times as much followed tempering to light straw, and little or none followed the second tempering, to light blue, though this caused considerable shrinking in both cases of first hardening.

In connection with the first tempering, to light straw colour, in both cases of second hardening, an interesting phenomenon was observed, as follows:—In all cases of tempering to colour, the bar was sandpapered bright, very slowly and uniformly heated, until the desired colour appeared, and then quenched in water at room temperature to arrest progress of tempering. But after this secondary quenching the bars continued to shrink measurably for several hours. The final, stable measurements are given in the Tables. Why no further shrinking occurred when the bars were tempered to light blue is not entirely clear; seemingly, the large shrinkage which followed first tempering, to light straw colour, brought about a condition sufficiently stable to withstand further change by the moderately higher temperature required for tempering to light blue.

With the object of adding to the research and also to demonstrate practically the phenomena in question, one of the authors of this paper (Hadfield), with the full concurrence and desire of the other (Brush), continued the research and carried out the following experiments at the Hadfield

Laboratory, Hecla Works, Sheffield. The following description shows the methods employed and the results obtained.

These experiments further prove the accuracy of the work described above. The more definite particulars regarding quenching temperatures and the correlation of hardness determinations will be of interest. These results are also presented in a somewhat different manner and form, attempts being made to obtain the actual evolution of heat by making suitable allowance for imperfections of the heat insulation. The steels selected were of the same composition and treatment as those previously referred to.

4 7	
Anal	VS18.

	C.	Si.	s.	P.	Mn.	Cr.	Ni.
(A)	0 -67	0 ·12 est.	0 ·0 <b>37</b> est.	0 ·027 est.	0 ·12 est.	2 .02	1 :98
(B)	0 :67	0 ·12 est.	0 ·037 est.	0 :027 est.	0 ·12 ent.	2 ·51	2 ·81

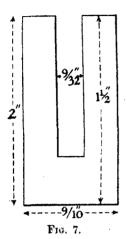
These two specimens represent what is termed the nickel-chromium type of steel, which is sensitive to hardening. Such material when quenched is intensely hard. Type B differs in containing higher percentages of nickel and chromium. The main constituents are carbon, nickel, and chromium. Silicon, sulphur, phosphorus, and manganese are low and have little or no influence. The chromium intensifies the hardening action of the carbon, as shown by one of the authors (Hadfield) in his paper to the Iron and Steel Institute in 1892 on "Alloys of Iron and Chromium." The nickel present toughers the material.

The importance of this subject to those engaged in what are termed hardening operations will probably be considerable. Neither of the authors pretends to claim that the curious facts now noticed are concerned with or relate to every fracture brought about by hardening. On the other hand, undoubtedly the phenomenon noticed is well worthy of study.

Nevertheless the phenomenon of hardening is most complex and even now a little understood one. Intense molecular stresses brought about by the hardening phenomenon introduce a very complex set of problems still to be solved; when it is considered that there are millions of small articles weighing from a few cunces to a few pounds each, which are now-a-days satisfactorily hardened, nevertheless there still remain mysterious phases. Besides, the hardening phenomenon becomes still more difficult to handle when reaching large masses, for example, objects such as those of 20 inches

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diameter or even more. In such cases it is necessary to suddenly convert thousands of cubic inches from a soft plastic mass into one of intense



hardness. Naturally phenomena are met with which are difficult of explanation, but this paper probably throws some light upon the dark corners which still remain.

#### Preparation of Specimens.

Cylinders of the form shown in fig. 7 were machined from bars carefully annealed at 770° C., and cooled slowly.

### Description of Apparatus.

After a few preliminary trial experiments, the following arrangement was made (fig. 8):-

Two vacuum flasks were placed side by side in a wooden box, and packed round with magnesia, the whole enclosed in a tin receptacle with more magnesia

in between, and loaded with lead. The tin, with its contents, was placed in a bath of running cold water to maintain a more steady surrounding temperature. The flasks were partly filled to a certain depth-equal in the two cases—with powdered fireclay. The rubber tube circulating the water

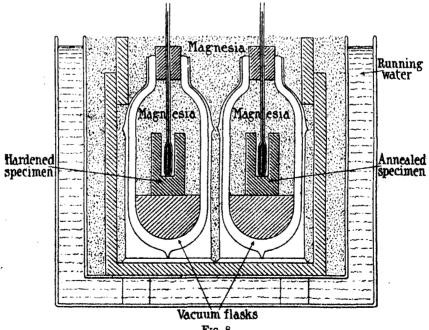


Fig. 8.

in the outer vessel was coiled round the corks of the two flasks, so as to cool the air in the neighbourhood to approximately the same temperature as the water.

# Method of Working.

A pair of specimens of the same steel were taken. One of these was cooled in running water and transferred to one of the flasks, a mercurial thermometer was placed in the piece and the flask filled up with magnesia, the water circulating round the apparatus. The second piece was heated to the desired quenching temperature and dropped into the quenching medium. After exactly 2 minutes it was taken out and placed as quickly as possible in the same running water as the previous specimen, its temperature being observed by a thermometer. When it had reached the same temperature as the other piece it was transferred immediately to the second flask, a similar thermometer being placed in the piece, the flask filled up and corked in a similar manner, with a layer of magnesia spread over the top of the flasks.

The height of the fireclay in the flasks was so arranged that the pieces were practically in the middle of the flasks.

In these experiments, the pieces were in position in the flasks and ready for observation at from 15 to 20 minutes after quenching. The temperature readings were taken at definite intervals, for several hours following, of the unhardened and hardened pieces, and also the surrounding air.

#### Results.

The observations obtained are shown in Tables III, IV, V and VI, and plotted on the top of figs. 9, 10, 11 and 12.

The difference of temperature between the two pieces was next plotted, and the rate of increase or decrease in temperature of both pieces at any instant deduced by calculation. From these rate observations it was possible to deduce the rate of evolution of heat in the quenched specimen, allowing for the radiation and conduction losses. This curve of evolution is shown by the broken line for each specimen at the bottom of the diagrams. They are compared with each other in fig. 13.

It will be observed that the method presented by one of the authors (Hadfield), as shown in fig. 9, is more clear, because, by dealing with rates of evolution of heat, corrections can be made for natural loss of heat due to imperfections in the heat insulation.

Table III.

Temperature of Oil Scleroscope: 85. Treatment: 940/790° C., Oil for 2 minutes. before Quenching: 29-9° C. After Quenching: 31.5° C. Ball Hardness of Specimen: 740. Time: 11 A.M. Specimen: 3137p. Date: 18.8.16.

Rate of evolution of heat by specimen.	Calories per gramme per minute.	0 0.805 0 0.9861 0 0.194 0 0.0194 0 0.0068 0 0.0088 0 0.0019 0 0.0012 0 0.0012 0 0.0012 0 0.0012
Rate of loss of heat by radiation and conduction.	Calories pa per m	0.0003 0.0013 0.0017 0.00175 0.00175 0.00187 0.00187 0.00187 0.00187 0.00187 0.00187 0.00183 0.00183 0.00183 0.00183
Factor connecting rate of change of temperature with	temperature above surroundings.	0.00143 0.00125 0.00125 0.00183
Average rate of change of temperature between	observations.	° C. per min. 0.08 0.036 0.018 0.002 0.002 0.002 0.002 0.001 0.0018 -0.0018 -0.0018 -0.0018 -0.0018 -0.0018 -0.0018 -0.0018 -0.0018 -0.0018 -0.0018 -0.0018
Change of temperature of quenched piece between	observations.	. C. 0.48 0.144 0.144 0.05 0.05 0.014 0.05 0.05 0.05 0.05 0.05 0.05 0.05 0.0
Difference in temperature between quenched and	pieces.	0 % C C C C C C C C C C C C C C C C C C
Temperature of quenched piece.		· 8 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4
Temperature of untreated piece.		. 888 888 888 888 888 888 888 888 888 8
Temperature of surrounding		。 \$\psi \psi \psi \psi \psi \psi \psi \psi
Time.	The state of the s	11.21.11.21.12.22.22.22.22.22.22.22.22.2

After a few hours the alope of the cooling curve of the hardened specimen gives approximately the rate of loss of heat to the surrounding flash, as the amount of heat being evolved is too small to affect our measurements. From this, the rate at which it was losing heat during the first part of the experiment was deduced by assuming Newton's Law, namely, that the loss of heat is proportional to the difference in temperature between the specimen and its surroundings.

rable IV.

Temperature of Oil Scleroscope: 82. After Quenching: 29.4° C. Ball Hardness of Specimen: 720. Time: 10.22 A.M. Treatment:  $910^{\circ}$  C., Oil, 2 minutes. Specimen: 16638. before Quenching: 27.8° C. Date: 15.8.16.

		···		-	***																					
Rate of evolution of heat by specimen.	r gramme inute,			0.0201	0.0207	#010.0	9900.0	2800.0	0.0028	0.0038	0.0003	88,000	0.000	7000-0-	<b>†</b> 000.0	0 .0021	6000-0	9000.0-	1000.0 0	0.0	0.0	1000	1000	9000-0-		•••
Kate of loss of heat by radiation and conduction.	Calories per gramme per minute.		9	000	0.000	0.00045	0.00055	0.00065	9,000.0	0.00085	0.00085	0.00082	6000-0	6005 5005 5005	60000	00000	6000.0	0.00085	8000-0	9000-0	0.00075	0.00075	2000.0	0 .00063		
ractor connecting rate of change of temperature	temperature above surroundings.				-			-1	T marrier er	eri Pir nome				ndrod rough			. exace. o	0.0012	0.00	46100.0	0.000	0.0000	0.00908	00000		0.00155
Average rate of change of temperature between	observations.	2	c. per min.	<b>7</b> 0.00	20.0	0.016	900.0	800.0	0.003	900 000	2000-0	0.0021	#000·0-	-0.0012	†000·0-	+0.0015	0.0	10000	0000	9000		9000	-0.0013			Mean
Change of temperature of quenched piece between	observations.	J°	 ئ ز	0.10	2 6	88	90-0	<b>8</b> 0.0	70.0 0.0	9 C	10.0	0.03	-0.01	-0.05	20.0	\$ 5 0 +	300	3 2	200	0.01	[0.0-	2 P	90	!		T mo
Difference in temperature between quenched and untreated	pieces.	0 0	0.0	0.10	<b>8</b> .0	<b>8</b> 8	0.43		0.52	0.22	99.0	0 C	99.0	0.56	\$ O	0.58	0.58	 0	0.23	0.21	<b>37.</b> 0		9 5	7		-
Temperature of quenched piece.		J .	19.50	19-60	19.70	97.61	, o	9.6	19 92	19-93	5. 5. 5. 5. 5. 5. 5. 5. 5. 5. 5. 5. 5. 5	0 × 01	86.61	19.86	19.79	19.78	19.76	71.61	02.61	20 S	90.67	00 00	50.51	26.61	17 -95	
Temperature of untreated piece.	**************************************	<u>.</u>	19.5	19.9	ic i	87. DI	24.61	19.40	19.40	88.61	2 0	19:30	08.61	19 :30	19 .52	19.50	19.18	71.61	77.61	7	10.11	13 11	10.15	9	17-80	-
Temperature of surrounding air.		Ö.	18.9	19.0	10 p	0.51	16.1	F. 61	19.6	30 o	0.55	9.5	9.61	19.7	19.0	19.0	19.02	8 8	77 61	00:01	13 50	- ti	- ox	9	8-21	
Time.			10.43	10.48	10.56	11.8	11.18	11.23	11.33	5.5	12.8	12.23	12.48	2.5	0.7	2.35	6.0	3	. A	202	25.00	9	6.30	16.8/16	9.45	

After a few hours the slope of the cooling curve of the hardened specimen gives approximately the rate of loss of heat to the surrounding flask, as the amount of heat being evolved is too small to affect our measurements. From this, the rate at which it was losing heat during the first part of the experiment was deduced by assuming Newton's Law, namely, that the loss of heat is proportional to the difference in temperature between the specimen and its surroundings.

heat by evolution of heat by and duction.  Calories per gramme	0.0503 0.03134 0.01134 0.01134 0.0006 0.0007 0.0006 0.0006 0.0006 0.0006 0.0006 0.0006 0.0006 0.0006 0.0006 0.0006 0.0006 0.0006 0.0006 0.0006 0.0006 0.0006 0.0006
Rate of loss of heat by radiation and conduction.  Calories per m	0 0001 0 0003 0 0003 0 0005 0 0 0 0005 0 0 0 0
Factor connecting rate of change of temperature with temperature above surroundings.	-0.0036 -0.0020 +0.0010 -0.0019 -0.0020 -0.0020
Average rate of change of temperature between observations.	C. Per min.  0 045  0 045  0 0484  0 013  0 003  0 003  0 003  0 000  0
Change of temperature of quenched piece between observations.	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
Difference in temperature between quenched and untreased pieces.	0.00 0.52 0.52 0.52 0.52 0.52 0.52 0.52
Temperature of quenched piece.	· ** ** ** ** ** ** ** ** ** ** ** ** **
Temperature of untreated piece.	。 \$2525252222222222222222222222222222222
Temperature of surrounding air.	。 % % % % % % % % % % % % % % % % % % %
Time.	0.0.0111111111111111111111111111111111

After a few hours the slope of the cooling curve of the hardened specimen gives approximately the rate of loss of heat to the surrounding flask, as the amount of heat being evolved is too small to affect our measurements. From this, the rate at which it was losing heat during the first part of the experiment was deduced by assuming Newton's Law, namely, that the loss of heat is proportional to the difference in temperature between the specimen and its surroundings.

Table VI.

evolution of heat by specimen. Temperature of 0 0002 0 0002 0 0003 0 003 0 0004 0 0007 0.0604 0.0258 0.0191 0 0133 0 0077 0 0076 0 0056 0 0036 0 0036 0.0009 Scleroscope: 85-87. Rate of 9100.0 Calories per gramme per minute. Rate of loss of heat by radiation conduction. 0.0002 0.0006 0.0010 0.0015 0.0015 0.0016 0.0016 0 0016 0 0016 0 0015 0 0015 0 0014 0 0014 and Treatment: 910° C., Water, 45 seconds. Water before Quenching: 18° C. After Quenching: 20.2° C. Ball Hardness of Specimen: 740. surroundings. temperature Factor connecting temperature rate of change of 0.00167 0.00265 0.00266 0.00313 0.0010 with 0.005 of change of temperature between Average rate observations. ° C. per min. 0.006 0.006 0.006 0.006 0.006 0.006 0.006 0.0 -0.0013-0.0053 -0.0007 -0.006 **200.0**+ Change of temperature of quenched piece between observations. quenched and Difference in temperature between untrested Time: 2.30 P.M. 1:00 0:00 Temperature of quenched Specimen: 1663s. Temperature of untreated 路路站 <u>x</u> <u>x</u> <u>x</u> Temperature eurrounding άcό す Date: 17.8.16. 18.8.16 Time. 6.30 6.45

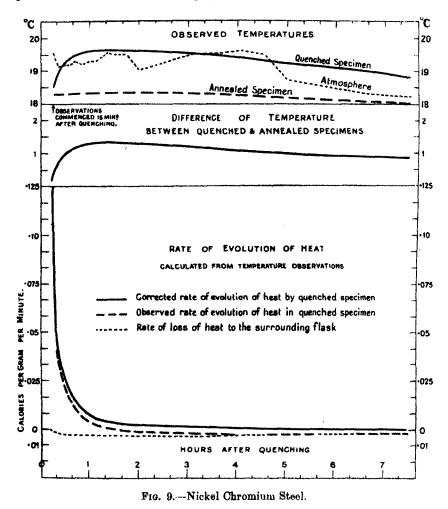
the amount of heat being evolved is too small to affect our measurements. From this, the rate at which it was losing heat during the first part of the experiment was deduced by assuming Newton's Law, namely, that the loss of heat is proportional to the difference in temperature between the specimen After a few hours the slope of the cooling curve of the hardened specimen gives approximately the rate of loss of heat to the surrounding flash, and its surroundings.

# Table VII.

							Rookoz	Date of lan	•
Temperature of surrounding	rature f nding	Temperature of untreated piece.	Temperature of quenched piece.	Difference in temperature between quenched and	Change of temperature of quenched piece	Average rate of change of temperature between	connecting rate of change of temperature	trate of toes of heat by radiation and conduction.	Rate of evolution of heat by specimen.
	*	•		pieces.	observations.	observations.	temperature above surroundings.	Calories per gramme per minute.	r gramme nuke.
<b></b>		۰۵.	ئ	ပ်	- C.	° C. per min.			
ergen a		18.3	1.81	2.0	ç	9			
		18 -3	18.1	<b>5.</b> 0	) )	P			
		80	18.1	٠ د د	, c			_	
		100 c		ç	00	0			
		5.01	1.01	9 9	0.0	0.0	,		
a-1-4400 -4		18 28	2 8 S	61.0	10.0-	-0.0052			
no, .		18:36	18.00	21.0	20 C	-0.002			
		18 25	18-06	0.18	100 0-0-0-0-0-0-0-0-0-0-0-0-0-0-0-0-0-0-	100-0-			
1		18 -23	18-09	91.0	200	200.00	1008	Too small to measure.	g <u>i</u>
Not taken	aken	18:32 5:45 18:45 1	999	%I.O	10.0	-0.001			
		18.17	2 ×	100	20.0-	-0.005			
		18.14	18	0.10	0.01	9000-0-			
		01.81	18-0	1.0	96	<b>0</b> 0	100		
		18.06	17.96	.0	9 6	> ç			
*.va*a		10-81	17-91		200	9000			
	-	17.88	17.85	8					
		17-90	17 98	01.0	90	-0.0003			
	•	5.75	12.4	3.	40.0-	-0.001			

#### Discussion of Results.

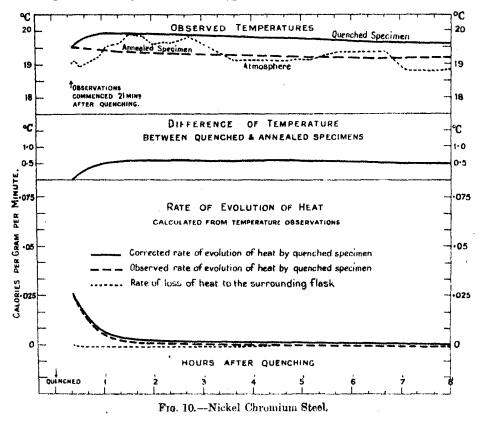
The apparatus is of a somewhat simpler nature than that used in the first experiments described in this paper. It was found, however, that the



mercurial thermometers used (graduated to one-tenth degree) are sufficient to demonstrate, and measure with an approximate degree of accuracy, the rate of evolution of heat. The apparatus could, no doubt, be still further

improved, with more perfect heat insulation, but an actual rise of temperature of 1.1° has been met with, and clearly noticed, in these experiments.

Generally, the preceding result, that the evolution of heat is very much more rapid immediately after quenching than later on, is confirmed; but in these particular experiments the apparatus did not enable detection of an



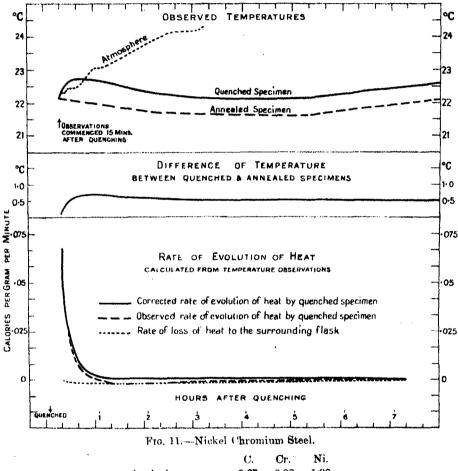
C. Cr. Ni.
Analysis ...... 0:67 2:02 1:98

Hardness after Quenching ...... Brinell hardness figure: 720. Scleroscope: 82.

evolution in any of the specimens after five or six hours. This is obviously a question of degree of perfection of the apparatus.

From the general trend of the curve it is apparent that the bulk of the heat was evolved almost immediately after quenching. The observations did not commence in any case less than 15 minutes after quenching, and by making arrangements to take records sooner, no doubt still better and more interesting results would be obtained.

Comparing the evolution of heat from the various specimens, taken with the 1663 steel (fig. 13), No. 4 is a repetition of No. 2. The curves are distinctly different: in No. 4, while roughly the same amount of heat appears to be evolved, the evolution seems to take place later than in No. 2, so that the

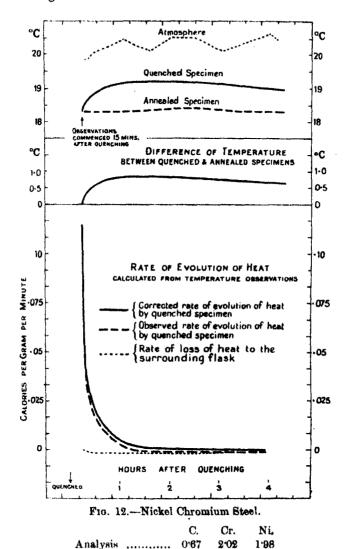


phenomena are not necessarily the same, even under similar conditions of quenching.

The water-quenched specimen (No. 3) shows a larger evolution of heat, as might be expected, than the specimen (No. 2) quenched in oil from the same temperature. The hardening in such cases is more rapid and more intense.

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The single specimen of 3137 D steel with higher chromium and nickel contents, and quenched from a different temperature to the 1663 specimen No. 2, shows the greatest heat evolution.



Further work would probably enable the observer to distinguish more particularly between the characteristics of the various steels.

The practical importance of these experiments is that they further

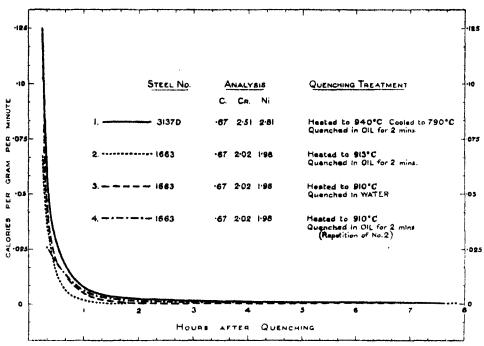


Fig. 13.—Rate of Evolution of Heat by Nickel-Chromium Steel after Quenching.

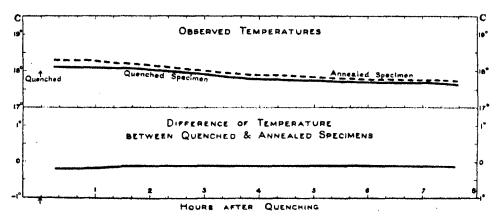


Fig. 14.-Nickel Chromium Steel.

	C.	Cr.	Ni.	
Analysis	0.6	7 2.51	2.81	
Quenching Treatment	Heated to 94	O' C., cool	ed in fur <mark>nac</mark>	e, specimen became
_	magnetic a	t 635° C.	Quenche	d at 615° C. in oil
	for two min	nutes.		
Hardness after Quenching	Bali hardness	figure: 3	08. Sclero	scope: 42. (In the
_	annealed co	ndition b	efore quenc	hing the ball hard-
	ness was 20	0, and sel	eroscope ha	rdness 39.)

demonstrate the very unstable state in which steel recently hardened really is, one practical indication of this being occasional spontaneous fracture.

The explanation of this interesting phenomenon is not very apparent. In searching for such an explanation it is important to distinguish between cause and effect. The most obvious explanation would be that the specimens in quenching necessarily do not cool at an equal rate all through their mass, since while losing heat the interior must always be higher in temperature than the exterior. It may be that the interior portion by cooling somewhat slower does not acquire quite the same degree of hardness, nor, therefore, expand to the same amount as the exterior. Some adjustment must, therefore, go on in the material, so that the comparatively softer and more duetile interior can accommodate itself by flow to the greater dimensions of the harder exterior portions. In stating this, it must not be considered that the difference in the interior hardness is great; under suitable conditions an interior hardness of equal intensity can be obtained. While the accommodation referred to takes place—it is supposed continuously for some time after quenching-internal work is being developed which would naturally be manifested as heat, and, under conditions of heat insulation as in these experiments, as a rise in temperature. Inability to adjust itself in this way owing to lack of duetility, would seem to explain the spontaneous fractures met with.

This theory is, however, somewhat discounted by the American results quoted, in which a distinct evolution of heat was measured in the absence of any change in dimensions.

Any chemical change inside the steel, that is to account for the evolution of heat noticed, would be expected to be probably accompanied by a change of hardness, which, however, does not appear to occur. Certainly there is no very vital change; it must be remembered, however, that present methods of measuring hardness do not enable us to precisely determine this point. It is for this reason that one of the authors (Hadfield) in his work on the Hardness Committee of the Institution of Mechanical Engineers, and also in his contribution to the discussion on that Report, called attention to the great desirability of improved methods being brought about of accurately determining the hardness of materials possessing hardness of from about 580 to 750 as now indicated approximately by the Brinell method. Excellent as is this method, it is not sufficiently accurate to give more than an approximate idea of such hardness. It may be here added that, at about 600 Brinell ball number, what is usually termed glass-scratching hardness commences.

As regards the practical bearing of this matter, as applied to industrial

practice, it is important to bear in mind that the rise of temperature found does not actually exist under practical conditions, even to the extent of 1°, as shown by one of our (Hadfield's) experiments; that is to say, under such conditions the heat evolved has every facility for getting away, and cannot take effect by raising the temperature of the steel. Certainly, as a fine point, there may be a very slight rise of temperature, say, in the centre of a large mass of steel, 15 or 20 inches in diameter, after hardening, because the heat has a long way to go to get from the centre to the outside, but on the quantities of heat demonstrated by these delicate experiments, this rise of temperature is negligible, and cannot, per se, do any harm. The special feature of these experiments is that they demonstrate the evolution of heat by allowing it to raise the temperature of the steel, which then becomes the outward and visible sign.

In other words, it is necessary to distinguish between cause and effect. The heat evolution itself must be only an effect. What the cause is, one of us (Brush) suggests in the remarks put forward earlier in this paper. No doubt breakages in large masses of steel are due partly to the expansion on hardening. Such large masses often do not harden in the centre of the mass, and, therefore, do not expand equally throughout the section. Unless such comparatively softer material can accommodate itself by stretching to the greater dimensions of the harder portions, there is great liability for fracture to occur.

In conclusion, the authors of this paper are led to regard the fact that hardened steel is in a condition of very great molecular strain, somewhat unstable, especially at first, after being quenched. Spontaneous relief of a small portion of the strain causes generation of heat until stability at room temperature is reached. Any considerable rise in temperature, as in tempering, permits further spontaneous relief of strain or molecular rearrangement, doubtless accompanied by more generation of heat, and so on until annealing is reached.

The authors desire to express their best thanks to Mr. S. A. Main, B.Sc., A.R.C.Sc.I., and Mr. T. H. Burnham, B.Sc., and others who have rendered assistance in regard to the preparation and analysis of the specimens of steel used and carrying out the various experiments and other valuable help.

# An Application of the Theory of Probabilities to the Study of a priori Pathometry.—Part II.

By Lieut.-Colonel Sir Ronald Ross, K.C.B., F.R.S., R.A.M.C.T.F., and Hilda P. Hudson, M.A., Sc.D.

## (Received October 19, 1916.)

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ERRATA IN PART I. ('Proceedings,' A, vol. 92.) Page.	
211, line 23, write Z/P for ZP.	
213, equation 17, omit factor $(1-x)$ .	
equation 18, omit factor $(L+1-2x)$ .	
line 23, omit "since $\frac{1}{2}(L+1)$ is greater than L."	
215, line 15, write $d\mathbf{Z}/dt$ for $d\mathbf{z}/dt$ .	
line 21, write $-(\mathbf{V}-\mathbf{N}-r)/(\mathbf{K}-\mathbf{V})$ for $-(\mathbf{V}-\mathbf{N}+r)$ .	
217, equation 29, write $x = L - (L' - L)/(y - 1)$ .	
218, line 22, write $V-v$ for $v-V$ .	
line 2 from bottom, write $\int \frac{2K\beta\epsilon^{-2K\beta t}}{y_0 - \epsilon^{-2K\beta t}} dt$ .	
219, equation 36, write $e^{-KLt}$ for $e^{-2KLt}$ .	
equation 38, write Po for P (twice).	
equation 39, write $e^{-vt}$ for $e^{-KL}$ and for $e^{-KL'}$ .	

Page.

221, line 8, last term, write L2 for L.

lines 4, 3 from bottom, write "seen that all the tangentials of x are zero."

222, lines 6, 5 from bottom write " $dx_0/dt = K(LP_0-1)/P_0^2$ , or nearly  $KL/P_0$ ."

223, line 10, write KL/P<sub>0</sub> for K/P<sub>0</sub>.

225, equation 67, write (1-L) for (-L).

229, equation 80, write  $x/x_0$  for  $L/x_0$ .

230, 3, write Part VI for Part IV.

## PREFACE TO PART II.

Part I of this paper was published in the 'Proceedings,' A, vol. 92 (1916), having been read on November 11, 1915. In June last, the Royal Society was kind enough to give a Government Grant for providing me with assistance in order to complete the paper, and for carrying on further studies upon the subject; and Miss Hilda P. Hudson, M.A., Sc.D., was appointed for the work from May 1, 1916. The continuation of the paper has accordingly been written in conjunction with her; and I should like to take the opportunity to express my obligations to her for her valuable assistance, especially in regard to Part III—which is to appear shortly.

I must apologise for the rather numerous small errors in Part I—due to the fact that the proofs were received by me when I was abroad on active service.

The entire paper here presented is still limited to the theoretical side of the subject, as defined in the Preface to Part I. Records of epidemics are now being examined in order to find how far the theoretical results which we have reached may be applied to them; but these studies must be reserved entirely for future discussion.—R. R.

#### VIII.

(i) Hypothetical Epidemics: Deduction of Constants.—In any case of independent happening we can use equations 8 and 12 with V, v, N, r, all zero. Then

$$dx/dt = h(1-x),$$
 and, if  $x_0 = 0$ ,  
 $ht = -\log_{\epsilon}(1-x),$   
 $= x + \frac{1}{2}x^2 + \frac{1}{3}x^3 + \dots$  if x is small,  
 $= 2.30 \log_{10} \frac{1}{1-x}$  for all values of x.

If the value of x is known for any value of t, say a year, this equation enables us to find h, and thence x for any other period, hour, day, week, etc.

Thus suppose that child-birth, death, or migration occurs to 20 per mille of a population of all ages during one year, to what proportion do they occur in one day? We have

$$365h = 0.02 + 0.0002 + 0.0000027 + \dots$$
  
 $h = 0.000055.$ 

To find the proportion for one hour, we divide by 24; and to find it for 7 or 30 days, we multiply by these numbers respectively.

Or suppose that 85 per cent. of plague cases, taken at any stage of the illness, die within 30 days, and we require the daily death-rate of such mixed cases. Then we have

$$30h = -2.30 \log_{10} (1 - 0.85),$$
  
$$h = 0.063,$$

giving a constant death-rate of 6.3 per cent. per diem. If the cases are all taken from the commencement of the illness, the curves are quite different, and show the highest death-rate some days after the onset—but this does not concern us at present.

If the annual birth-rate is 30 per mille, and the annual death-rate is 20 per mille, then the corresponding daily rates are

$$n = 0.000083$$
 and  $m = 0.000055$ .

Hence if the immigration and emigration rates counterbalance each other we may take for the daily variation element v = n - m = 0.000028.

In this example the increase of the population at the end of the year would amount to 1 per cent.—that is, P would vary from  $P_0$  at the beginning of the year to 101  $P_0$  at the end of it. But if we use the value of v just given for equation 13, namely,  $P = P_0 e^{vt}$  (putting t = 365 and vt = 0.0103), we obtain  $P = 1.0103 P_0$  at the end of the year—which is a little greater than the figure just given. The reason for this is, of course, that in equation 13 we assume that the propagation is continuous—that is, that during the year the progeny of the original population will themselves have progeny. But this is not assumed in the value of P first obtained.

We may also calculate v from equation 13 if we know the values of  $P_0$  and P at the beginning and end of t. Thus the population of England and Wales was 10,164,256 in 1811, and 36,070,492 in 1911. Then since  $vt = \log_{\epsilon} P - \log_{\epsilon} P_0$  and  $t = 365 \times 100$ , the daily variation-element is v = 0.0000347, the yearly variation-element is 0.012666, and the ten-yearly variation-element 0.12666. If a population doubles itself in a period t, we

have  $vt = \log_{\bullet} 2 = 0.693$ , so that at the above rate the English population ought to double itself in 19,975 days, or nearly 55 years—which is about the case.

If the daily death-rate of plague is taken at the figure just calculated, of 0.063, and the plague birth-rate is a normal one of 30 per mille a year (so that N = n), then V = N - M = -0.063; so that, if v = 0.000028, v - V = 0.063... daily. Such figures give us some concrete ideas of what the constants are likely to be in cases of human epidemics. [Compare Sections III and V (iii).]

The reversion-element r is particularly elusive since we seldom have known figures regarding it to deal with. It is best to proceed as we did in connection with equation 20, and to assume that 90 per cent. of the affected individuals revert in the time t, where  $t=1, 2, 3, \ldots, 10$ , or more years.

Then for a daily element  $365 r = \frac{1}{t} 2.30$ . Hence if 90 per cent. of the cases

revert in one year, the daily reversion-element is r = 0.00631. Thus the reversion-element is likely to be large compared with v or N and correspondingly important, and will be by no means negligible even when the considered disease is one in which the acquired immunity is supposed to be very lasting [compare Section III (iii)]. For a case reverts not only when it becomes again capable of showing a recognisable infection, but when it is again able to harbour the infective agents sufficiently to afford them a nidus whence they may infect others; and it is quite possible and indeed probable that this may often occur much earlier than we imagine. Thus persons vaccinated against smallpox may acquire the disease in a very mild and modified form after only a few years, and may then infect non-protected persons in full force; and there is no proof that a mild first attack of measles or other diseases may not give quite as short-lived an immunity that is, that those who have had the disease in infancy may not comparatively early acquire it again in an indistinguishable form and then spread it. In such cases, r may be considerably larger than we might otherwise expect.

Regarding immigration and emigration, it will suffice to note that in 1911 there were 350,429 immigrants into the United Kingdom and 454,527 emigrants from it.

Further remarks on the constants will be found in Section X.

(ii) We may now proceed to consider numerical examples of proportional happenings. For this purpose it is convenient to adopt the suggestion made towards the end of Section VII (vi), and to take c as a function of an independent parameter  $\gamma$  which is such that when  $\gamma$  is positive KL is positive and x always increases with the time, and when  $\gamma$  is negative KL is

negative and x always diminishes with the time (Section IX). We shall also write D for v-V and R for N+r. The principal constants of x and f may then be written

$$c = D + (\gamma + 1) R,$$
  $K = (\gamma + 1) R,$   $KL = \gamma R,$   $L = \frac{\gamma}{\gamma + 1},$   $l = c \frac{\gamma}{(\gamma + 1)^2}$   $\lambda = \frac{(\gamma + 1)^2}{4\gamma}.$ 

The reader is reminded that KL is the coefficient of l in x, the proportion of affected individuals (equation 50), and that the x-curve reaches its centre of symmetry when  $x = \frac{1}{2}L$ , and its maximum value L when t is very large [Section VII (iii)]. The period at which x reaches its centre of symmetry and dx/dt reaches its maximum is  $t = \tau = \frac{1}{KL} \log_e \frac{L-x_0}{x_0}$ . If  $x = 1/P_0$  and  $LP_0$  is large compared with unity, then, as suggested in connection with equation 58, we may now write

$$\gamma R \tau = \log_{\epsilon} P_0 + \log_{\epsilon} \gamma - \log_{\epsilon} (\gamma + 1),$$

and at twice this period the maximum number of affected individuals less one is reached.

Similarly, when t is very large, the ultimate value of the proportion of new cases is l. But if  $L > \frac{1}{2}$ , f rises to a previous maximum value  $\frac{1}{4}c$  when  $x = \frac{1}{2}$ , and thereafter falls to its ultimate value l [Section VII(v)]. The ratio between the maximum and the ultimate value is  $\lambda$  (equation 67). The period at which the maximum value is reached is

$$t = \tau' = \frac{1}{KL} \log_{\bullet} \frac{1}{x_0} \frac{L - x_0}{2L - 1}$$

(equation 66); and when  $x_0 = 1/P_0$  and LP<sub>0</sub> is large, this may be written

$$\gamma R \tau' = \log_{\bullet} P_0 + \log_{\bullet} \gamma - \log_{\bullet} (\gamma - 1).$$

But this maximum of f (previous to its ultimate value) occurs only if  $\gamma > 1$ .

It is evident that when c is expressed as a function of  $\gamma$  in this manner, K, KL, L,  $\tau$ ,  $\tau'$ , and  $\lambda$  are independent of v and V, and that l contains them only as parameters of c.

On the other hand,  $\tau$  and  $\tau'$  are functions of the original population  $P_0$  and increase as it increases—because, obviously, x and f require a longer period to reach their corresponding values if the population is large. It is convenient therefore to adopt a definite figure for  $P_0$  in the following Table; and we put  $P_0 = 10,000$ , which is, say, the population of an ordinary town. We may also assume that unity is negligible compared with LP<sub>0</sub> unless  $\gamma < 0.1$ 

If Po is not 10,000, but some multiple or fraction of it, say 10,000 p, all

Table of Hypothetical Epidemics.

Ex. No.	۸	ıi	~;	ż	Reversion	on rate 90 R = (	Reversion rate 90 per cent. per annum. $R=0.0064$ .	annum.	ř.	Reversion rate negligible. $R=0.00083$ .	te negligib 00083.	ei.
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91	10,000	10001	10001	2500	64.1	1	0.14	3	0.835	1	11	0.83

we have to do to find  $\tau$  and  $\tau'$  is to add to or subtract from the figures given in the corresponding columns of the Table the quantity  $\log_{\bullet} p/\gamma R$ . Thus, if  $P_0 = 1000$ , we subtract  $2\cdot30/\gamma R$ . As  $\gamma$  increases above 100,  $\tau$  and  $\tau'$  approximate more and more closely to the value  $\log_{\bullet} P_0/\gamma R$ ,  $\tau$  being always less than this and  $\tau'$  greater than it.

The actual curves depend largely on the values of R. If we suppose the case of a human disease, of which the affected birth-rate N equals the natural birth-rate n, which is taken at 0.000083 daily, corresponding, according to the previous sub-section, with an annual birth-rate of 30 per mille—then R equals the former figure if r is so small as to be negligible. But if r is a daily rate corresponding to an annual reversion of 90 per cent., it will amount to as much as 0.0063, so that R = 0.0064. We will suppose that these two values of R are a minimum and a maximum.

Now if we suppose also that c=1, that is, that each affected individual daily infects or reinfects one other individual, then we have  $\gamma = (1-D)/R-1$ . That is, if D=0,  $\gamma=12{,}000$  if R is a minimum, and  $\gamma=155{,}5$  (or roughly 150) if R is a maximum. Thus, if the infection rate is near unity, the value of  $\gamma$  will reach from three to five figures, and the epidemic will resemble the last examples given in the Table.

In Example 1, if the population remains the same during the whole of this long period (which is, of course, never likely to occur), only about ten living persons out of the 10,000 will be found unaffected at the end of it; and the ultimate and maximum daily number of new cases  $lP_0$  reaches only 0.00083, that is, only one new case in 3.3 years.

If, however, R has its maximum value, there is one new case in about sixteen days.

In Example 4, half the population is ultimately affected, but still f has no maximum before its ultimate value. When, however, in Example 5  $\gamma$  increases above unity, this maximum begins to appear, and the ratio  $\lambda$  between the maximum and ultimate values of f constantly increases with  $\gamma$ . At the same time,  $\tau$  and  $\tau'$  diminish and approach each other.

If c is nearly unity,  $\tau' = 2.30 \log_{10} P_0 = 9.2$  days, and f reaches its maximum in a short time, whatever the value of R. More generally, if D = 0,  $c = (\gamma + 1)R$ , and if  $\gamma$  is large (say over 50),  $\gamma + 1 = \gamma$  roughly, and  $\tau = 1/c$ .  $\log_e P_0$ . In other words, if  $\gamma$  is considerable, not only does L = 1 nearly, but the maximum ( $\frac{1}{2}c$ ) of f and the mode, or time ( $\tau'$ ) when that maximum is attained, depend roughly on c only, the population being fixed.

If  $L > \frac{1}{2}$  the f-curve slopes downward from its summit more slowly than it rose towards that summit. Put  $x = \frac{1}{2} + \xi$ , then  $f = c(\frac{1}{4} - \xi^2)$ , and has the same value for equal and opposite values of  $\xi$ .

But 
$$\left| \frac{df}{dt} \right| = 2c \left| \xi \right| \frac{d\xi}{dt}; \quad \frac{d\xi}{dt} = \frac{dx}{dt} = \frac{K}{c} f - K (1 - L) (1 + \xi),$$

and is less when  $\xi$  is positive than when  $\xi$  has the equal and opposite value. Hence, at two points of the f-curve whose ordinates are equal, the descending side is less steep than the ascending side.

Since  $f = \frac{c}{K} \frac{dx}{dt} + c(1-L)x$ , and the first term on the right gives a perfectly symmetrical bell-shaped curve, we may call c(1-L)x the excess of the f-curve. When D = 0 and  $\gamma$  is considerable, the excess varies roughly from  $\frac{1}{2}R$  at the centre of symmetry to R, when t is very large—that is, roughly, from  $\frac{1}{2}l$  to l. Both of these become small when r, the reversion-rate, is small.

The important result, therefore, follows that, if also c is near unity, and therefore  $\gamma$  is large—that is, if the infection-rate is high while the reversion-rate is low—then the f-curve becomes a nearly symmetrical bell-shaped curve. This, according to Dr. Brownlee (Section I), is just the kind of curve presented by epidemics of certain zymotic diseases. The prima facic inference is therefore that such epidemics may be wholly or chiefly mere cases of proportional happening, as defined in Section VII (i). It is even the case that, in such diseases, the fall of the curve is often more slow than its rise, as happens with the f-curve.

When  $\gamma$  is large and L = 1 nearly, the two changes of curvature of the curve occur, according to equation 65, when  $6x = 3 \mp \sqrt{3}$ , that is, when (equation 53)

$$\gamma Rt = \log_{\epsilon} P_0 + \log_{\epsilon} (1/x - 1),$$
  
=  $\log_{\epsilon} P_0 - 1.32$  and  $\log_{\epsilon} P_0 + 1.03,$ 

the latter being nearer to the summit than the former.

(iii) Several methods may be employed for calculating the curves of x, f, Z and F in detail. The simplest is to divide the period during which x varies from  $x_0$  to  $\frac{1}{2}L$  into a number (say 10) of equal parts and then to calculate the ordinate of the curve at each section. In equation 58 we used  $\tau$  to express this interval when  $x_0 = 1/P_0$ , but it may be employed more generally to express the abscissa of the centre of symmetry, when  $x_0$  has any value, so that  $KL\tau = \log_{\epsilon}(L/x_0-1)$ . We now put  $t = \tau T/10$ , give to T the successive values 1, 2, 3, ..., 10, and calculate the corresponding values of x, namely  $x_1$ ,  $x_2$ ,  $x_3$ , ..., and so on. Thus we have from equations 50

$$x_{\rm T} = L\{1 + \sqrt[10]{(L/x_0 - 1)^{10 - {\rm T}}}\}^{-1}$$

The root can be easily evaluated by means of logarithms, and the value of

x then obtained from a table of reciprocals (e.g., as in Barlow's Tables). Owing to the symmetry of the x-curve, its values when T lies between 10 and 20 can be easily found—for example  $x_{13} = L - x_7$ . When we have ascertained the ordinates of x, we can quickly calculate those of f from equation 61, and, unless the case-mortality is high, we can generally assume for short and sharp epidemics that the original population remains constant and that  $Z = xP_0$  and  $F = fP_0$ . It will be observed that, by this method, when  $\tau$  has been first calculated we need subsequently deal only with the values of L and of  $L/x_0-1$ . Thus suppose that L=1 nearly, that P=10,000, and that  $x_0=1/P_0$ , then we have approximately,

This is, of course, an ultimate case where f is quite symmetrical—so that, for example  $f_7 = f_{13} = cx_7x_{13}$ .

Another useful method for calculating x and f is to transfer the origin to the centre of symmetry (equation 56). But if the ordinates are required for successive natural units of time, such as days or weeks, in order to compare them with statistics of epidemics in which such units have been used, then we must of course give to t the successive values 1, 2, 3, ..., and calculate the ordinates directly from equations 50. Here the symmetry of x will not be so useful, because the centre of symmetry is not likely to coincide with any one of the periods of time for which the ordinates have been found. It will, therefore, be generally easier to plot the curve by the method first indicated, to measure off the natural units of time along the time-axis, and then to estimate the corresponding ordinates geometrically.

## IX.

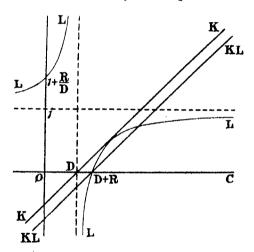
"(i) Hypometric Happening: KL Negative.— We have hitherto always supposed that the happening-element is constant during the whole of the considered period, but it is now necessary to examine the changes which will be produced in the functions by certain changes in this element. We here study only the cases of dependent happenings already discussed, and these only for hypometric happening. It is no longer very useful to take c as a function of  $\gamma$ .

In Section VII (vi), while considering the constants K, L, c, we saw from

equations 50 that if KL is positive, x always increases and is therefore always greater than  $x_0$ , its value when t = 0. This implies that c > D + R. When this inequality becomes an equality, KL vanishes and  $dx_0/dt = 0$ , that is, x remains near its original value, when t is not very large, so that the happening may be said to be isometric [see (v) below]. When, however, c < D + R, KL becomes negative; and it is seen from equations 50 that, as  $e^{-KLt}$  then always increases with the time, x always diminishes, and must therefore be always less than  $x_0$ .

We call such cases hypometric happening. That is, we now suppose that, after having been greater than D+R, c becomes less than it, or even zero. What, then, will be the nature of the curves?

The solutions of equations 44, 45, 47, 51, 52 remain valid for all real values of c, and we have therefore only to interpret results already known.



It is first necessary to examine K, KL, and L more particularly as functions of c, but we shall do so only in the case when D is positive (injurious happenings) or zero. Then D, R are positive constants. We have

$$K = c - D$$
,  $KL = c - D - R$ ,

represented by parallel straight lines meeting the axis of c at an angle of  $45^{\circ}$  on the positive side of the origin,

$$L = 1 - R/(c - D)$$
, or  $(L-1)(c-D) = -R$ ,

and the graph of L is a rectangular hyperbola, with asymptotes L=1, c=D, dotted lines in the figure, parallel to the axes of co-ordinates.

The last portion of this L curve, for c > D + R, gives cases of hypermetric happening already studied; but we have to consider the range  $0 \le c < D + R$ ; since L becomes infinite when c = D, we have to consider the two portions:

 $0 \le c < D$ , for which L is positive and greater than 1; and D < c < D + R, for which L is negative.

(ii) First let c=0; that is, suppose that the happening suddenly ceases altogether, while all the other elements remain the same. It is advisable to use marked letters for the quantities after this event. We take it then that when the original happening c ceases, t'=0, and that the values which x, Z, P, had reached up to this time are now expressed by  $x_0'$ ,  $Z_0'$ ,  $P_0'$ , while x', Z', P' denote these functions as t' increases. Similarly, K' and L' are now the values of K and L without the element c. Then, since K'=-D, equations 51 and 52 become

$$\Gamma' = P_0' \epsilon^{vt'} \left\{ 1 - \frac{x_0'}{L'} (1 - \epsilon^{-(D+R)t'}) \right\}, \tag{81}$$

$$Z' = Z_0' \epsilon^{(V-R)t'}. \tag{82}$$

As V-R=-M+I-E-r, Z' decreases from its original value  $Z_0'$  or Z, and ultimately approaches zero—unless the immigration is greater than the sum of the other elements (as may happen in a war area)—and its diminution is more rapid when M, E, r are large. With regard to equation 81, we observe that  $P_0'\epsilon^{vt'}$  is the natural increase of the population, living when the happening ceased, after that event; and the equation shows that P' equals this quantity less a function of t' which is zero when t'=0, which increases with t', and which finally slowly approaches the limit  $x_0'/L'$ .  $P_0'\epsilon^{vt'}$  when t' is large. That is to say, the population which remained when the happening ceased continues to suffer from its effects for some time afterwards, and then finally reaches the value

$$P' = P_0' e^{vt'} (1 - x_0'/L').$$

Here  $x_0'/L'$  is always less than unity, for  $x_0'$  is the value of x at the moment when the happening ceased, and this could not have been greater than L, which is less than unity [Section VII (vi)], while, as shown in the previous sub-section, L' is greater than unity when c = 0. Hence P' is always less than  $P_0'e^{ct}$ , and the difference gives the loss of population due to the cases which continue after the happening ceased.

The fraction  $L'/x_0'$  occurs in the denominator of x' in equation 50. As it is greater than unity, the coefficient of  $e^{-K'L't'}$  is positive, so that x' always diminishes as t' increases—as could have been already inferred from equations 81 and 82.

(iii) The next case is when c' is some quantity between zero and D (which is generally very small). For the study of this case, the first of equations 50 may be written

$$x' = x_0' \left\{ \frac{x_0'}{L'} + \left( 1 - \frac{x_0'}{L'} \right) e^{-\mathbf{K}'\mathbf{L}'\mathbf{l}'} \right\}^{-1}, \tag{83}$$

which diminishes indefinitely as t' increases. If c' = D and L' is consequently infinite, this becomes  $x_0 \epsilon^{\mathbf{k'} \mathbf{L'} t'}$ , which vanishes.

The values of P' and Z' are easily obtained from equations 51 and 52, if we remember that the indices D/K' and c'/K' are now negative. When c' = D, the expressions for P' and Z' become indeterminate, but can be easily evaluated, and we have

$$P' = P_0 e^{vt'-q}$$
, where  $q = x_0' D(1 - e^{-Rt'})/R$ .

(iv) When c' lies between D and D+R, K' is positive and L' is negative, and varies from  $-\infty$  to zero. Then it will be seen from equation 83 that x' is still positive, and, as in the previous cases, diminishes indefinitely as t' increases. For it may be written

$$x' = x_0' \left\{ e^{-\mathbf{K}'\mathbf{L}'t'} - \frac{x_0'}{\mathbf{L}'} e^{-\mathbf{K}'\mathbf{L}'\mathbf{T}'} - 1 \right\}^{-1}$$
(84)

where K'L' is negative. For P' we have

$$P' = P_0' e^{vt'} \left\{ 1 - \frac{x_0'}{L'} (1 - e^{K'L't'}) \right\}^{-D/K'},$$
 (85)

which is also always positive since L' is negative, and increases without limit when t' is large. P' is less than,  $P_0'e^{rt'}$ , because the effects of the original happening continue to be felt by the population after the happening itself has been reduced from c to c'.

(v) When c' = D + R exactly, L' and KL' = 0, and, when t' is small,  $x = x_0'$  nearly, and the happening may be said to be *isometric*. The values of x' and P' become indeterminate, but can be ascertained by finding the limits when L' = 0 of the expressions in equations 84 and 85, so that

$$x' = \frac{x_0'}{1 + x_0' K't'},$$

$$P' = P_0' e^{vt'} (1 + x_0' K't')^{-D/K'}.$$

Or the same equations can be obtained by integrating equation 47 after putting L=0 in it, and then integrating both sides of equation 44. In this case also, then, x' tends to decrease as t' increases, and finally approaches zero, when t' is very large.

(vi) If K'L' is positive, however small it may be, x' always increases, as already seen in Section VII (iii).

It must be remembered that, though x', the proportion of affected individuals, diminishes, this does not mean that new cases cease to occur. On the contrary, unless c is absolute zero, f' is the same function of x' as before. And rx' expresses, as before, the reversions of the old cases.

When D = 0, the phase described in (iii) above is suppressed, and we

begin, when c' = 0, at the point when K' = 0, K'L' = -R, and  $L' = -\infty$ , and the functions will be easily understood.

### X.

(i) Parameter Analysis.—We have now considered x, f, and P as functions of the time, but it remains to examine how they vary if we give different values to the parameters h, r, v, V, n, m, i, e, N, M, I, E. The symbol l has been used to denote the limit of f when t is very large. This is an important quantity in disease happenings because it gives the number of new cases which continue to occur when x has reached its limit, that is, after epidemic manifestations have ceased. It is, by hypothesis, these final new cases which keep the infection alive permanently in the population; we may call l the endemic ratio. First consider l as a function of r

$$\frac{\partial l}{\partial r} = \frac{c}{K} (2L - 1) = \frac{c}{K^2} (c - D - 2R).$$

Thus l is positive when r = 0 (if KL > 0) and increases with r until this reaches a value which makes  $L = \frac{1}{2}$  and  $l = \frac{1}{4}c$  [Section VII (vi)]. After this l diminishes as r increases. But if c - D > 2R then r never reaches this value and l always increases. Thus l considered as a function of r has forms similar to those of f considered as a function of t.

The behaviour of l as a function of c is of the same nature. A similar procedure applies to f and P.

The effect upon the total population P due to variations in the parameters is important. The fundamental equation is 44:

$$dP/dt = vP - DxP.$$

As P and x are always positive, the sign of dP/dt depends on v and D. If D=0, the happening is equivariant and the natural change of population due to v is not affected. If D is negative, the happening is beneficial and the natural change of population is augmented by it. If D is positive, the happening is injurious and the natural change is reduced. If v-Dx is negative, especially when x=L, the total population will diminish indefinitely.

It is found that  $\partial P/\partial r$  is always positive; that is, in infectious diseases, a quicker loss of affectedness, including loss of immunity, is beneficial. This may seem surprising until we reflect that, as v > V, the longer the affectedness continues in the individual the greater will be the loss of life due to it, since we generally suppose in such cases that M > m and that these elements act during, not one, but every time-unit lived by the affected part of the population. Of course, the greater r is the more quickly on the average will affectedness, including immunity, be lost.

Next,  $\partial P/\partial c$  is zero or negative, and the higher the infection rate the more injurious is the happening.

 $\partial P/\partial V$  is zero when t=0. It generally increases at first with t and afterwards decreases; it is negative when x=L provided 1-c(1-L)/K is negative. In other words, in these cases an increase of V is beneficial at the beginning of the outbreak, but injurious later on. Now V=N-M+I-E and diminishes if the case-mortality M increases; in fact  $\partial P/\partial M=-\partial P/\partial V$ . Thus an increase in the case-mortality is injurious at first, but may be ultimately beneficial, because an affected individual who dies ceases to be infective.

An Application of the Theory of Probabilities to the Study of a priori Pathometry.—Part III.

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### XI.

(i) Variable Happening.—In Section IX, we commenced by touching upon the necessity of studying the effect of changes in the happening-element, but there dealt only with the case of hypometric happening. We now proceed to examine other changes in this element.

It is unlikely that in any infectious disease the infectivity-element c will always remain constant. It may remain practically such for some length of time; and the hypothetical results of this condition have therefore been analysed above in detail; but nature abhors a straight line, and we may infer from general experience that changes are sure to occur from time to time. As suggested in Section I, changes in infectivity may be due—

- (a) to the action, so to speak, of the infecting organisms themselves—which is difficult to believe in because it involves the conception that organisms living in large numbers of different hosts should, as it were, make a kind of concerted and simultaneous effort; and
- (b) to changes in season, climate, or other environment which may (1) increase or diminish the infective strength of the infecting organisms; or (2) facilitate or hinder their transference from one host to another.

At present we can proceed only on the supposition that the change has occurred, without attempting to enquire how or why it has occurred; and only some brief notes on the subject can be given at present.

(ii) Discontinuous Change.—We have hitherto supposed that when t=0 the number of affected individuals is  $Z_0$ , which may be small or large. If the happening is hypermetric (KL>0) and  $Z_0$  is less than LP, the number of affected individuals, Z, will increase towards the latter figure; but if the happening is isometric (KL=0), or is hypometric (KL<0), Z will diminish to the limits discussed in Section IX. What will happen if the infectivity is suddenly changed during one unit of time from c to c', and thereafter remains at the latter figure?

If c' > c, the x-curve suddenly becomes steeper; x itself is continuous, but its gradient is discontinuous. The f-curve is discontinuous, and has a sudden rise at the moment when c changes; thereafter both curves proceed according to the equations with c' substituted for c. If at the moment of discontinuity more than half the population is affected, so that f is descending, there is an epidemic manifestation, a sudden rise followed by a decline. Both L and l are increased.  $\bullet$ 

These are probably just the conditions which apply to many zymotic diseases, in which most of the population appears to remain affected, that is immune, for years or permanently. In these cases, at the moment of discontinuity x is nearly L, and L is nearly unity, and the augmented infectivity c' acts merely upon the small residue of non-affected individuals, let us say, newly-born infants, or children, or others who have hitherto escaped infection by accident or by residence in remote villages. It is well known that at the beginning of the present war recruits from many highland villages were attacked by very virulent measles on joining camps

in the lowlands. On the other hand, the same sort of epidemic may occur in numbers of villages and small towns in which the considered infection has died out from want of material, and so allowed of a gradual accumulation of fresh material, which is then suddenly fired (so to speak) by the entry of one or two infective cases from outside.

It is extremely improbable, of course, that the infectivity actually makes a single per saltum change; but we may still apply the equations already obtained if we give to c a series of progressive discontinuous augmentations for successive units of time, followed by similar discontinuous diminutions until c returns to its original value. In this case the f-curve will again show epidemic manifestations (if  $x > \frac{1}{2}$ ), and will then decline again towards a lower value. This is one way of approximating to a continuous change in c.

(iii) Continuous Variation.—We may, however, obtain new equations on the hypothesis that the infectivity c is a continuous function of the time. Let us suppose that  $c = \phi'(t)$ , where  $\phi'(t) = d\phi(t)/dt$ . Then in the fundamental equation 47, namely dx/dt = Kx(L-x), we have

$$K = \phi'(t) - D$$
 and  $KL = \phi'(t) - D - R$ .

Put x = 1/y, so that dy/dx = -KLy + K; then

$$y \exp \int \mathbf{K} \mathbf{L} dt = \int (\mathbf{K} \exp \int \mathbf{K} \mathbf{L} dt) dt + \text{constant}$$

by the well-known solution. As however, K = KL + R,

$$\int (K \exp \int KLdt) dt = \exp \int KLdt + R \int (\exp \int KLdt) dt;$$

hence

$$y = 1 + \exp\left(-\int_0^t \mathbf{K} \mathbf{L} dt\right) \left\{ R \int_0^t \left(\exp \int_0^t \mathbf{K} \mathbf{L} dt\right) dt + y_0 - 1 \right\}.$$

If R is negligible, as may often happen in short and sharp epidemics with long immunity, we may write, for many diseases at least,

$$\int KLdt = \phi(t) - Dt,$$

$$x = \frac{1}{1 + \cosh k \times e^{-\phi(t) - Dt}}.$$

We have at present no knowledge of the nature of the function  $c = \phi'(t)$  or even if there is such a function. But if there is, we may suppose that, for positive values of t,  $\phi'(t)$  is small when t is small, increases at first as t increases, reaches a maximum for a certain value of t, and then declines to a small value again when t is larger—as is observed in many phenomena. In other words we should expect a symmetrical or non-symmetrical bell-shaped curve such as those with which we are familiar in statistical work.

(iv) Graphical Treatment of x.—We may also suppose that c is given in terms of the time t, not by an analytic function, but by a curve whose equation

is unknown. We can then determine the nature of x and f by graphical methods.

Since dx/dt = Kx(L-v), there could only be a turning value of x when K = 0 or x = 0 or x = L. But when K = 0, then KL = -R and dx/dt does not vanish; when x = 0 the happening ceases altogether; the only turning value of x is when x = 1.

Now since by definition x lies between 0 and 1, we can only have x = L if L also lies between 0 and 1; the diagram of IX (i) shows that this only occurs when c > D + R. Hence unless the given c-curve rises above the level D + R. the corresponding x-curve has no fluctuations, and either rises steadily to 1 as its limit, or sinks to 0. But wherever the c-curve has a portion rising above D+R, we can plot the values of L = 1-R/(c-D) corresponding to this portion, which form a cap, part of the L-curve, lying entirely between the levels 0 and 1. If the c-curve fluctuates, there are a series of these L-caps, which are the only parts of the L-curve that the x-curve can possibly cross.

Now, whenever the x-curve meets an L-cap, x = L, dx/dt = 0, and x has a turning value. If the x-curve descends to meet the L-cap from outside, it begins to ascend as soon as it is inside; and goes on ascending till it meets

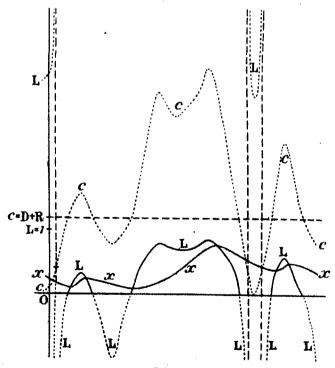


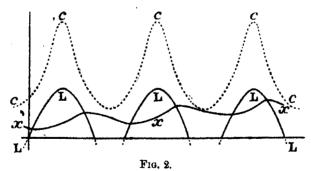
Fig. 1.

the opposite side of the same cap, when it passes outside and immediately begins to descend, until it meets another L-cap. The v-curve descends steadily except where it is inside a cap; and as soon as the L-caps are plotted, the general character of the curve is fairly apparent. If c has a definite limit  $c_{\infty}$  when  $t \to \infty$  and this limit is less than D + R, then the last L-cap is closed, v is ultimately descending and tends to 0. But if  $c_{\infty} > D + R$ , then L has a limit  $L_{\infty}$  and v tends to the same limit as L, and may approach it either from above or from below.

Since L = 1 - R/(c - D),  $\partial L/\partial c = R/(c - D)^2$ , and is positive, L rises and falls with c and the top of an L-cap corresponds exactly to a maximum of c. But a maximum of x occurs where it crosses a descending branch of L: hence the maxima of x occur somewhat later than the corresponding maxima of c.

Suppose, for example, that c is periodic, rising and falling regularly every year, and crossing the level D+R twice a year. Then L has a series of caps with equal equidistant maxima of height  $\lambda$ , say. Start from a minimum of c, between two L-caps, and suppose the value  $x_0$  of x to be given.

Then x begins to descend. If  $x_0$  is large, x may pass over the top of one or more L-caps, descending all the while, but, sooner or later, it meets an L-cap, passes inside it, and begins to rise. It thereafter meets every cap, for it leaves each cap at a height less than  $\lambda$ , and, since it descends between the caps, it cannot pass over the top of the next. Every year x rises and falls, the maximum occurring later than that of c or L, and we have a yearly epidemic. But there is no reason to make these epidemics equal; though, if any two are equal, they all must be. For if x has equal values for corresponding points of the periods, the whole course following these points is the



same; in other words, if two periods are superposed, and if the two parts of the x-curve have one point in common, they coincide, but, if x meets any L-cap at a point lower than the preceding cap, its whole course inside that cap is lower, and lower still in the next cap, and so on, tending to a limiting form which is periodic, and which may be the axis itself, the happening

dying out. But, if x meets any L-cap higher than the last, it meets the next higher still, and so on, and tends to a periodic limiting form of finite fluctuations.

In order to plot x more closely, we have to replace the fundamental differential equation by the approximate difference equation

$$x_{n+1} - x_n = \mathbf{K} x_n (\mathbf{L} - x_n),$$

where K, L are calculated from the value of c measured off the given curve, and  $x_0$  is given; or by some modification of the method.

(v) Graphical Treatment of f.—If c is given and w has been obtained, we have next to deal with f, which can be directly calculated from the equation

$$f = cx(1-x) = c\left(\frac{1}{4} - (x - \frac{1}{2})^2\right) = c\left(\frac{1}{4} - (\frac{1}{2} - x)^2\right).$$

Hence f always increases with c: as x increases, f increases if  $x < \frac{1}{2}$ , and decreases if  $x > \frac{1}{2}$ . If we wish to know the general behaviour of f, the following Table is useful; it allows for a single bell of each of the c- and x-curves, the maximum of x occurring later than that of c.

		f.			
<i>r.</i>	æ.	if $x < \frac{1}{2}$ .	if $x = \frac{1}{2}$ .	if $x > \frac{1}{2}$ .	
minimum	decreasing	decreasing	minimum	increasing	
increasing	decreasing	P	increasing	increasing	
increasing	minimum	increasing	increasing	increasing	
increasing	increasing	increasing	increasing	?	
maximum	increasing	increasing	maximum	decreasing	
decreasing	increasing	P	decreasing	decreasing	
decreasing	maximum	decreasing	decreasing	decreasing	
decreasing	decreasing	decreasing	decreasing	P	
minimum	decreasing	decreasing	minimum	increasing	

In using this, we follow f down a column until x passes through the value  $\frac{1}{2}$ , when we cross to the next f-column.

Since in each column f is increasing in the third row and decreasing in the seventh, there is bound to be a maximum of f between them, which occurs before the maximum of c if  $x > \frac{1}{2}$  and after if  $x < \frac{1}{2}$ .

Recrulescence.—It is seen that if c and w are both decreasing and  $w > \frac{1}{2}$ , we cannot say what f is doing, as the two causes of its change act in opposite

ways. It is possible for f to have a minimum followed by a short rise and a maximum, and, if x then becomes equal to  $\frac{1}{2}$ , f falls again to another minimum. This would happen, for example, if c suddenly became constant after decreasing, before x drops to  $\frac{1}{2}$ . Then we have a slight recrudescence of the epidemic near its close.

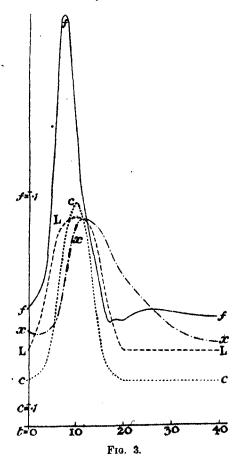
Since 
$$\frac{df}{dt} = \frac{\partial f}{\partial c} \frac{dc}{dt} + \frac{\partial f}{\partial x} \frac{dx}{dt}$$

and in the case considered dc/dt and dx/dt are both negative,

$$\frac{df}{dt} = -x(1-x) \left| \frac{dc}{dt} \right| + c(2x-1) \operatorname{K}x(\mathbf{L} - x)$$

and is positive, so that f rises again, provided dc/dt is small enough, but, as x decreases, the factor 2x-1 decreases and changes sign; the positive second term in df/dt becomes negative, and f sinks.

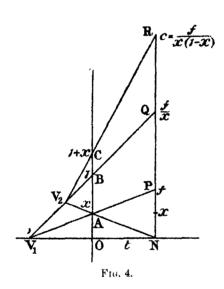
In fig. 3, c rises and falls in a symmetrical bell and then remains constant;



L does the same; x has an unsymmetrical bell, rising more steeply than it falls, and sinking to the same limit as L; and f shows an epidemic with slight double recrudescence before sinking to its limit.

The graphs of c, x, and L are on the same scale, and that of f on 10 times the scale.

(vi) f Assigned.—The last sub-section started by assuming that c is given in some experimental way. But c is not given except by conjecture, and the method is useful to test whether any particular conjecture leads to numerical results which agree with the records of actual epidemics. Now the most extensive and accurate records are the notifications of fresh cases and of



deaths made by the medical officers of health; in particular, the records of measles in Aberdeen for the 20 years 1883–1902 are very suitable material, though even there the numbers are not large enough to be quite satisfactory.

The death-rates do not correspond to any of the symbols we have introduced so far; for MZ is the number of deaths of affected persons per unit time, a different thing from the number of deaths due to the affection. We return to this in a later section.

We start therefore with the fresh assumption that the notifications, that is, the values of F, are known.

Suppose also that P is given, either by interpolation from census returns, or because in a short and mild epidemic P is nearly constant. Then f is known as a function of t. The fundamental equations are best taken in the forms

$$dx/dt = f-x(D+R-Dx),$$
  $c = f/x(1-x),$ 

from which c and c can respectively be determined, if reasonable estimates can be made of the constants D, R.

When x, f, are found and plotted, we can construct c graphically. P is the point (t, f). Along the vertical axis mark off

$$OA = x$$
,  $OB = 1$ ,  $OC = 1 + x$ ; then  $AB = 1 - x$ ,  $AC = 1$ .

Let PA meet the axis NO in  $V_1$ ; let  $V_1B$  meet PN in Q and NA in  $V_2$ , and let  $V_2C$  meet PN in R.

QN/OB = PN/OA, QN = 
$$f/x$$
,  
RN/AC = QN/AB, RN =  $f/x(1-x) = c$ ,

so that R is the point on the c-curve corresponding to P on the f-curve.

If D and R can both be neglected, then

$$x = \int_{t=0}^{t} \mathbf{F} dt + v_0.$$

In this case, x steadily increases whatever is the law of f, and the area under the f-curve always < 1.

In a great many cases, the f-curve is a slightly unsymmetrical bell, rising more steeply than it falls. Now

$$x^{2}(1-x^{2})\frac{dc}{dt} = \frac{df}{dt}x(1-x) - f^{2}(1-2x),$$

and df/dt is positive for the first, smaller part of the range, then vanishes and is negative for the rest of the time. The second term is negative if  $c < \frac{1}{2}$ , and positive if  $x > \frac{1}{2}$ .

Now if  $x_0$  is small, at the summit where df/dt = 0,  $x < \frac{1}{2}$  and dc/dt is negative. In this case, the c-curve reaches its summit sooner than that of f, and is more unsymmetrical. But if  $x_0$  is larger, 1-2x changes its sign earlier, and the summit of the c-curve is later in consequence. These results are an extension of those in Part I (p. 224), where we found that in the same case where D, R, are neglected, f is perfectly symmetrical when x is constant.

But if we do not wish entirely to exclude reversions, we assume

$$D = 0, R > 0.$$

Then

$$dx/dt + Rx = f,$$

$$x = e^{-Rt} \int_{t=0}^{t} f e^{Rt} dt + x_0 e^{-Rt}.$$

For example, let f = at(T-t), which is the simplest function that rises and falls, vanishing at t = 0 and t = T, with a maximum at  $t = \frac{1}{2}T$ . Then

$$x = \frac{at}{R^2} \left\{ R(T-t) + 2 \right\} - \frac{a}{R^3} (RT+2)(1-\epsilon^{-Rt}) + x_0 \epsilon^{-Rt}$$

Or we may allow for asymmetry by an exponential factor;  $f = at(T-t)e^{-\lambda t}$ , which still vanishes at t = 0 and t = T, but has a maximum before  $t = \frac{1}{2}T$ ;

$$x = \frac{at}{(R-\lambda)^2} \left\{ (R-\lambda)(T-t) + 2 \right\} e^{-\lambda t} - \frac{a}{(R-\lambda)^3} \left\{ (R+\lambda)T + 2 \right\} (e^{-\lambda t} - e^{-Rt}) + \alpha_0 e^{-Rt}.$$

If f is periodic, let

$$\begin{split} f &= a + b \sin pt, & \text{where } a \ge b; \\ x &= \frac{a}{R} (1 - \epsilon^{-Rt}) + \frac{b}{p^2 + R^2} (R \sin pt - p \cos pt + p\epsilon^{-Rt}) + x_0 \epsilon^{-Rt}. \end{split}$$

In all these, the negative exponentials decrease rapidly; in the last, x oscillates about a/R as mean, the phase lagging behind that of f by  $\frac{1}{p} \tan^{-1} \frac{p}{R}$ . Then c has the same period.

(vii) More General Equations.—In many diseases, for example those in which there is a period of incubation, the infectivity is variable, and depends not only on the absolute time but also on the duration of the case, which is the time elapsed since the case was first infected. In order to take this into account, c must be considered as a function of two independent variables, t the time, and s the duration; fluctuations of the infectivity of the disease as a whole cause c to vary as a function of t; episodes in the course of a single case cause c to vary as a function of s, very possibly a discontinuous function. For example, an incubation period of q days is represented by taking c = 0 when s < q.

For greater generality, suppose that V, I, E, M, N, c, r, D, R, all depend on t and s; but v, i, e, m, n on t only.

Let  $F_{t,\theta}dt$  be the number of fresh cases occurring between times t and t+dt.

Let  $F_{t+s,s}dt$  be the number of the batch of  $F_{t,s}dt$  cases which survive, having neither died, emigrated, nor reverted, at time t+s, being then of duration s. Thus  $F_{t,s}$  is the number of cases existing at time t whose duration is s. The total number of cases existing at time t is

$$Z = \int_{s=0}^{\infty} F_{t,s} ds. \tag{86}$$

As before, P = Z + A, and the number of fresh cases is now

$$\mathbf{F}_{t,0} = \frac{\mathbf{A}}{\mathbf{P}} \int_{s=0}^{\infty} c \mathbf{F}_{t,s} ds.$$

The rate of change of the particular batch of cases which started at time  $t_0$  is given by

$$\frac{d}{dt} \mathbf{F}_{t, t-t_0} = (\mathbf{V} - \mathbf{N} - r) \mathbf{F}_{t, t-t_0}$$

which may be written

$$\left(\frac{\partial}{\partial t} + \frac{\partial}{\partial s}\right) \mathbf{F}_{t,s} = (\mathbf{V} - \mathbf{R}) \mathbf{F}_{t,s}$$

$$s = t - t_0.$$
(87)

where

The fundamental equations now take the forms

$$\frac{d\mathbf{P}}{dt} = v\mathbf{A} + \int_{s=0}^{\infty} \mathbf{V} \mathbf{F}_{t,s} ds$$

$$\frac{d\mathbf{Z}}{dt} = \int_{s=0}^{\infty} (\mathbf{V} - \mathbf{R}) \mathbf{F}_{t,s} ds + \mathbf{F}_{t,0}$$

$$\frac{d\mathbf{A}}{dt} = v\mathbf{A} + \int_{s=0}^{\infty} \mathbf{R} \mathbf{F}_{t,s} ds - \mathbf{F}_{t,0}$$
(88)

These equations are not independent. If 87 is integrated with respect to s from 0 to  $\infty$ , since  $F_{t,\infty} = 0$  we have

$$\frac{d}{dt} \int_{s=0}^{\infty} \mathbf{F}_{t,s} ds - \mathbf{F}_{t,0} = \int_{s=0}^{\infty} (\mathbf{V} - \mathbf{R}) \, \mathbf{F}_{t,s} ds,$$

which is equivalent to 88 by virtue of 86.

These equations as they stand are quite unwieldy, but they are capable of being applied to a large number of simpler cases.

If V, R, are independent of t and constant for a particular range of s, say  $s = q_1$  to  $q_3$ , then for any intermediate value of s, from 87

$$\mathbf{F}_{t,s} = \mathbf{F}_{t-q_1, q_1} \epsilon^{(\nabla - \mathbf{R})(t-q_1)}$$

and if V, R have other constant values V', R' from  $s = q_2$  to  $q_3$ , then for any value of s in the latter range,

$$\begin{split} \mathbf{F}_{t+s} &= \mathbf{F}_{t-q_1, q_2} \, \epsilon^{(\mathbf{V}' - \mathbf{R}') \, (t-q_2)} \\ &= \mathbf{F}_{t-q_1, q_1} \, \epsilon^{(\mathbf{V}' - \mathbf{R}') \, t + (\mathbf{V} - \mathbf{V}' - \mathbf{R} + \mathbf{R}') \, q_2 - (\mathbf{V} - \mathbf{R}) \, q_1}, \end{split}$$

and so on.

The simplest case is when c is constant from  $s = q_1$  to  $q_2$ , zero for all other values of s, and independent of t, while all the other elements are neglected. Since there are then no deaths nor recoveries,  $F_{t,s} = F_{t,0}$  and P is constant. Then

$$\begin{aligned} \frac{dZ_t}{dt} &= \mathbf{F}_{t,0} = c \frac{\mathbf{A}}{\mathbf{P}} \int_{s=q_1}^{q_2} \mathbf{F}_{t-s,0} ds \\ &= c \left(1 - \mathbf{Z}_t / \mathbf{P}\right) \left(\mathbf{Z}_{t-q_1} - \mathbf{Z}_{t-q_2}\right), \end{aligned}$$

the suffixes showing the value to be substituted for t in Z.

Let  $c(1-Z_t/P) = Y_t$ , then this difference equation takes the simpler form

$$\frac{d\mathbf{Y}_t}{dt} = \mathbf{Y}_t(\mathbf{Y}_{t-q_1} - \mathbf{Y}_{t-q_2}).$$

The best way of dealing with this equation is to assume a Dirichlet series for Y, substitute and equate coefficients.

Let 
$$Y_t = B_0 + B_1 e^{-pt} + B_2 (B_1 e^{-pt})^2 + B_3 (B_1 e^{-pt})^3 + \dots$$

and let  $\Delta_n = \epsilon^{nq_1} - \epsilon^{nq_1}$ ,

then p,  $B_1$  are arbitrary,  $B_0 = p/\Delta_1$ , and the general reduction formula for the coefficients is

$$-B_n p(\Delta_n - n\Delta_1)/\Delta_1 = B_{n-1}\Delta_1 + B_{n-2}B_2\Delta_2 + B_{n-3}B_3\Delta_3 + \dots + B_{n-1}\Delta_{n-1}.$$

Since  $\Delta_n - n\Delta_1$  is positive, the signs of the coefficients alternate;  $B_0 = Y_{\infty}$  and is essentially positive, and therefore p is positive;

$$B_1 = -\frac{1}{p} \frac{dY_{\infty}}{dt} = \frac{c}{Pp} \frac{dZ_{\infty}}{dt}$$

and is positive, for Z always increases. Therefore  $B_{2n}$  is negative and  $B_{2n+1}$  positive.

The series for F is

$$\mathrm{F}_{t,0} = \frac{\rho \mathrm{P}}{c} \left\{ \, \mathrm{B}_1 \epsilon^{-pt} + 2 \, \mathrm{B}_2 (\mathrm{B}_1 \epsilon^{-pt})^2 + 3 \, \mathrm{B}_3 \, (\mathrm{B}_1 \epsilon^{-pt})^3 + \dots \, \right\}.$$

#### 'XII.

(i) Mortality: First Modification of the Equations of Part I.—It has been assumed that the average death-rate of the affected population is a constant M; part of this, m say, is due to other causes, and M-m is due to the disease. If m is constant, so is M-m, and the deaths from disease are simply proportional to Z and their ratio to the total population P is proportional to x. It therefore increases steadily; this does not agree with the records.

It is more reasonable to assume that the deaths from the disease all occur soon after infection and that their number is proportional to F; let it be  $\mu F$ . Then its ratio to the total population is  $\mu f$ , and rises and falls in proportion to f. This is much more nearly true. But now the fundamental equations are altered. We assume that the  $\mu F$  deaths are in addition to MZ deaths due to other causes, and that they all happen before the cases have had time to infect an appreciable number of other people. Then

$$dP/dt = VZ + vA - \mu F,$$
  

$$dZ/dt = (V - N - r)Z + (1 - \mu)F,$$
  

$$F = cZA/P.$$

As before write

$$Z = xP$$
,  $A = (1-x)P$ ,  $F = cx(1-x)P$ ,  $v-V = D$ ,  $N+r = R$ .

The result of elimination is

$$dx/dt = -\{D + R - (1 - \mu)c\}x + \{D - (1 - 2\mu)c\}x^2 - \mu cx^3$$
  
=  $-\mu cx(x - \alpha)(x - \beta)$ , say, where  $\alpha > \beta$ ,

of which the integral is

$$e^{-\mu c a \beta (a-\beta)t} = x^{a-\beta} (x-\alpha)^{\beta} (x-\beta)^{-\alpha} / \{x_0^{a-\beta} (x_0-\alpha)^{\beta} (x_0-\beta)^{-\alpha}\}.$$

The form of this curve depends on the signs of  $\alpha$ ,  $\beta$ .

Let 
$$Q = \mu c (x - \alpha)(x - \beta)$$
$$= \mu c c^2 - \{D - (1 - 2\mu)c\}x + D + R - (1 - \mu)c.$$

Case (i).—If the last term is positive,  $(1-\mu)c < D + R$ , then  $\alpha$ ,  $\beta$ , have the same sign; and if  $x_0$  is a small positive quantity, less than  $|\alpha|$  or  $|\beta|$ ,  $dx_0/dt$  is negative, x begins to decrease, Q cannot change sign and x decreases steadily to zero as its limit.

Case (ii).—If the last term in Q is negative,  $(1-\mu)c > D+R$ , then  $\alpha$  is positive and  $\beta$  is negative. When x=1, Q=R and is positive; therefore  $0 < \alpha < 1$ . Now  $dx_0/dt$  is positive, x begins to increase, but it does not reach  $\alpha$  till  $t=\infty$ ; hence Q cannot change sign and x increases steadily to  $\alpha$  as its limit.

Now f = ax(1-x), and as x varies from 0 to 1, f varies from 0 to 0 in a bell-shaped curve with a maximum at  $x = \frac{1}{2}$ .

In case (i) f decreases steadily from  $f_0$  to 0, in a curve of the same general character as the x-curve, for the factor (1-x) does not vary much.

In case (ii) if  $\alpha < \frac{1}{2}$ , f increases steadily to  $c\alpha (1-\alpha)$  as its limit, but if  $\alpha > \frac{1}{2}$ , f has a maximum  $\frac{1}{2}c$  when  $\alpha = \frac{1}{2}$  and then sinks to its limit  $c\alpha (1-\alpha)$ .

If D, R are both negligible,  $Q = c(x-1)(\mu x + 1 - \mu)$ , and  $\alpha = 1$ ; then f has a maximum and sinks to 0 as its limit.

(ii) Second Modification.—A popular assumption about infectious diseases is that the case ceases to be infective after a certain time, when also there ceases to be danger of death from the disease, but remains immune permanently. To represent this, suppose the population P to consist of three classes: P = A + X + Y, where A are unaffected, X infective and immune, Y immune. For simplicity, neglect all "natural" variations, but suppose there are MX deaths from the disease per unit time, rX recoveries, and F = rXA/P fresh cases. The fundamental equations are

$$dP/dt = -MX$$
,  $dX/dt = cXA/P - (M+r)X$ ,  
 $dY/dt = rX$ ,  $dA/dt = -cXA/P$ .

Hence P decreases and Y increases steadily. Suppose  $Y_0 = 0$ . Then

$$dY/dP = -r/M, Y = (r/M)(P_0 - P);$$

$$dA/dP = c/M \cdot A/P, A = A_0(P/P_0)^{c/M};$$

$$-(1/M)dP/dt = X = (1 + r/M)P - (r/M)P_0 - A_0(P/P_0)^{c/M};$$

$$dt = -\frac{1}{M} \int_{P=P_0}^{P} dP/\{(1 + r/M)P - (r/M)P_0 - A_0(P/P_0)^{c/M}\};$$

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which is integrable in finite form if c/M is rational, and leads to algebraic functions and logarithms.

In the final steady state, X = 0 and P is given by

$$(1+r/M) P - (r/M) P_0 - A_0 (P/P_0)^{r/M} = 0$$

which has a real root  $P_{\infty}$  between  $P_0$  and 0. A definite number of persons  $A_{\infty} = A_0 (P_{\infty}/P_0)^{e/M}$  escape the disease altogether.

Now, dX/dt is of the same sign as cA - (M+r)P, and is positive at first, provided  $c > (M+r)P_0/A_0$ ; in this case X, the total number of infective persons, rises to a maximum before sinking to 0.

dx/dt is found to be of the same sign as  $(c-M)A - rP_0$ , which is positive at first if  $c > M + rP_0/A_0$ , and steadily decreases.

 $d\mathbf{F}/dt$  is of the same sign as  $c\mathbf{A} - (\mathbf{M} + r)\mathbf{P} - (c - \mathbf{M})\mathbf{X}$ , and, if  $r > \mathbf{M}$ , this is less than  $d\mathbf{X}/dt$ ; the maximum of F (if it has one) is therefore earlier than that of X or of  $\mathbf{M}\mathbf{X}$ , that is to say, the greatest number of deaths occurs later than the height of the epidemic, which is the time of greatest number of notifications.

For example, let

$$r = 0.01, \quad M = 0.02, \quad c = 0.04, \quad r_0 = 0.0102.$$
Then
$$A_0/P_0 = 0.9898. \quad \text{Let } P/P_0 = p,$$

$$Mt = \int_{p=1}^{p} \frac{dp}{0.9898 p^2 - 1.5 p + 0.5} = \frac{-1}{0.52} \log_* \left\{ \frac{2.02 p - 1}{0.98 p - 1} \cdot \frac{-0.02}{1.02} \right\}$$

$$p = \frac{1 + 51 e^{-0.0104t}}{2.02 + 49.98 e^{-0.0104t}}$$

 $P_{\infty} = \frac{1}{2}P$ ,  $A_{\infty} = \frac{1}{2}P_{\infty}$  approximately.

X is stationary when  $A = {}^{8}P$  or 1/p = 1.32, leading to t = 300 approximately, the time which elapses before the maximum of the mortality.

## XIII.

(i) Discussion.—In the foregoing work, very little attention has been paid to the actual values of the constants. We have rather been preparing apparatus which can be used in a great variety of special cases.

It will be seen that the number of dependent variables is large, and that a fluctuation in any one can be accounted for in a great many different ways by supposing that there is a suitably adjusted variation in almost any one of the parameters. And the variation of any one parameter when it is over a range small compared with the mean value can be represented approximately by one of several analytic functions, which would lead to the most diverse results if the variation were to continue over a wider range. It is therefore

extremely rash to rule out a priori any one possible cause of fluctuation of any one phenomenon.

The cases already considered have led exactly to the series of curves required by the facts:

- 1. The steadily rising curve of a happening that gradually permeates the whole population [VII (iii)].
- 2. The symmetrical bell-shaped curve of an epidemic that dies away entirely [VII (v)].
- 3. The unsymmetrical bell of a new happening that begins with an epidemic, and settles down to a steady endemic level [VII(v)].
- 4. The periodic curve with regular rise and fall due to seasonal disturbances [XI (iv)].
- 5. The more irregular curve where there is recrudescence before the end of an epidemic, or where outbreaks differing in violence occur at unequal intervals [XI (v)].

This suggests that, as was stated in the Preface of Part I, the rise and fall of epidemics as far as we see at present can be explained by the general laws of happenings, as studied in this paper.

The methods which have been used call, however, for the following remarks:—

- A. In the equations of Section VII, the case-mortality and infectivity were both regarded as constants. It is very unlikely that this is strictly true; and it is much more probable that their values are highest at some definite short period after infection and then gradually die away.
- B. In Section XI some attempt is made to meet this objection by introducing the case-duration as a second independent variable, in addition to the time, but there are innumerable other considerations that may also be taken into account, such as the age, sex, and social position of the patients, climate, temperature, and, in the case of insect-borne diseases, the habits of the carrier.
- C. Except in XII (ii), the whole population has been divided into two classes only, the unaffected, and the affected who are considered to be both infective and also immune. But it is again unlikely that this is strictly true, and, in order to represent the facts accurately, a much larger number of classes would have to be considered.
- D. Although it would probably be easy to write down equations on any given hypothesis as to the number and behaviour of the variables, these equations, like those of XI (vii), would probably be quite unsuited to numerical work, and we should have to fall back on laborious approximatemethods such as expansion in series or mechanical quadratures.

E. The quantities x and L have been treated as continuous functions of the time, but, as they represent numbers of persons, they can only take integral values, and must be discontinuous unless they are constant; in the same way, f and l can only vary by integral multiples of 1/P. This is a serious drawback when the numbers are not large. In a small village, the average number of cases in the period between two epidemics may be only two or three, and, if these are removed by any chance, the whole course of events is entirely changed; there is no one to keep alive the infection, and a new generation may grow up entirely non-immune. Then the entry of a fresh source of infection has the same effect as if c rose suddenly from 0 to its normal value. In fact, in the case of small populations, other than the most probable values may often obtain, so that the whole of this paper is applicable to large numbers rather than to small ones.

The Initial Wave Resistance of a Moving Surface Pressure.

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1. The study of the water waves produced by the motion of an assigned pressure distribution over the surface has hitherto been limited to the steady state attained when the system has been moving with uniform velocity for a very long time. In his latest series of papers on water waves, Lord Kelvin\* made an elaborate graphical and numerical study of cognate problems, and expressed the hope of applying his methods to calculate the initiation and continued growth of canal ship-waves due to the sudden commencement and continued application of a moving, steady surface pressure.

In the following paper, I have not attempted any analysis of the surface elevation itself, but I have proceeded directly to the calculation of the corresponding wave resistance. At present the wave resistance is known only for the steady state for certain localised pressure systems in uniform motion, and it seems desirable to attempt some estimate of the time taken to attain this state when we take into account the beginnings of the motion. One might examine the effect of initial acceleration, but I have limited the problem by considering only the case of a system which is suddenly established, and is at the same instant set in motion with uniform velocity.

<sup>\*</sup> Kelvin, 'Math. and Phys. Papers,' vol. 4, p. 456 (1906).

The work is arranged in the following order: a general expression for the wave resistance as a function of the time, an exact solution for a certain waveless system, a comparison of this solution and the group approximation, and an approximate solution for certain systems which leave regular waves in their rear.

2. Consider, first, the effect of a single impulse applied to the surface of deep water, with no initial displacement of the surface. Take the axis of y vertically upwards, the axis of x horizontal, and the origin in the undisturbed surface. If the impulse is given by F(x), and if the Fourier method is applicable, the elevation at any time t is given by

$$-\pi y \rho y = \int_0^\infty \kappa V \sin(\kappa V t) d\kappa \int_{-\infty}^\infty F(\alpha) e^{i\kappa(x-\alpha)} d\alpha, \tag{1}$$

where  $V = (g/\kappa)^{\delta}$ , and the real part of the integral is to be taken. The effect of a pressure system, whether stationary or moving, can be obtained by integrating (1) suitably with respect to the time. For the pressure system may be considered as a succession of impulses; to each impulse there corresponds a fluid motion with definite velocity potential, and the velocity potential of the fluid motion at any instant is the sum of the velocity potentials due to all the previous impulses. Similarly, the corresponding surface elevations are simply superposed, and we obtain the required solution by an integration.

For a pressure system moving with uniform velocity c, we have to substitute x+ct for x in (1) and then integrate with respect to t between the limits 0 and t. But the solution so obtained is indeterminate to a certain extent, for we can superpose on it any infinite train of waves of wave velocity c. The so-called practical solution is found by choosing the amplitude of this train so as to annul the main regular waves in front of the travelling system. The integrals are, in fact, indeterminate, and are evaluated by taking their principal value, in Cauchy's sense of the term. Another way of avoiding this difficulty is to introduce small frictional terms proportional to the velocity. The integrals are then determinate, though more complicated in form; however, the final results, after the analysis is completed, can be simplified by taking the frictional coefficient as small as We shall use this method, and it is sufficient for our purpose to write, instead of (1),

$$-\pi g \rho y = \int_0^\infty e^{-\mu ct} \kappa V \sin(\kappa V t) d\kappa \int_{-\infty}^\infty F(\alpha) e^{i\alpha(x-\alpha)} d\alpha, \qquad (2)$$

where, ultimately,  $\mu$  is to be considered small.\*

<sup>\*</sup> Compare Lamb, 'Hydrodynamics,' p. 406.

Consider, then, a pressure system

$$p = \mathbf{F}(x), \tag{3}$$

which is suddenly established, and is at the same instant set in motion with uniform velocity c along the axis of x.

Putting x = w + ct, the surface elevation at any time t after the start is given by

$$-\pi g \rho y = \int_0^t e^{-\mu c u} du \int_0^\infty \kappa \nabla e^{i\kappa (\varpi + c u)} \sin \left(\kappa \nabla u\right) d\kappa \int_{-\infty}^\infty F(\alpha) e^{-i\kappa \alpha} d\alpha. \tag{4}$$

For simplicity, we shall confine ourselves to pressure systems which are symmetrical with respect to the origin; so that

$$\phi(\kappa) = \int_{-\infty}^{\infty} F(\alpha) e^{-i\kappa \alpha} d\alpha = 2 \int_{0}^{\infty} F(\alpha) \cos \kappa \alpha d\alpha.$$
 (5)

Also we shall use only localised distributions for which the integrals are finite and determinate; the systems will be finite and continuous and such that the integral pressure is finite, that is, the integral  $\int_{-\infty}^{\infty} F(\alpha) d\alpha$  convergent. Carrying out the integration with respect to u, we obtain

$$-2\pi g \rho y = \int_{0}^{\infty} \kappa \nabla \phi(\kappa) e^{i\kappa \omega} \left\{ \frac{1}{\kappa (\nabla + c) + i\mu c} + \frac{1}{\kappa (\nabla - c) - i\mu c} \right\} d\kappa$$
$$-e^{-\mu ct} \int_{0}^{\infty} \kappa \nabla \phi(\kappa) e^{i\kappa \omega} \left\{ \frac{e^{i\kappa (\nabla + c)t}}{\kappa (\nabla + c) + i\mu c} + \frac{e^{-i\kappa (\nabla - c)t}}{\kappa (\nabla - c) - i\mu c} \right\} d\kappa. \tag{6}$$

The first integral represents the steady state, while the second gives the deviation from it when we take into account the beginning of the motion.

3. From the first integral in (6) we have, with  $\kappa_0 = g/c^2$ ,

$$-\pi g \rho y = \kappa_0 \lim_{\kappa \to 0} \int_0^\infty \frac{\kappa \phi(\kappa) e^{i\kappa w} d\kappa}{\kappa(\kappa_0 - \kappa) + \mu^2 - 2\mu \kappa i}.$$
 (7)

The integral is to be evaluated first, before we make  $\mu$  zero, otherwise it is indeterminate. The interpretation for certain types of localised pressure system is well known; in such cases the solution takes the form

$$y = f(\mathbf{w}), \quad \mathbf{w} > 0,$$

$$y = -\frac{2\kappa_0}{q_0} \phi(\kappa_0) \sin \kappa_0 \mathbf{w} + f(-\mathbf{w}), \quad \mathbf{w} < 0.$$
(8)

This solution represents an infinite train of regular waves in the rear of the moving system, together with a disturbance symmetrical fore and aft which becomes negligible at a distance depending upon the concentration and the velocity. For our present purpose, all the examples we use are included under the case

$$\phi(\kappa) = \kappa^n e^{-\alpha \kappa}, \quad n > 0, \quad \alpha > 0.$$
 (9)

To verify the solution (8) in this case, regard  $\kappa$  in (7) as a complex variable  $\pi e^{i\theta}$ .

For w positive, integrate round a sector of radius R bounded by the lines  $\theta = 0$  and  $\theta = \beta$  ( $0 < \beta < \frac{1}{2}\pi$ ). Under the specified conditions, it can be shown that the integral along the arc r = R tends to zero as R is made infinite. In this way the integral (7) is transformed into an integral, along the line  $\theta = \beta$ , in which we can make  $\mu$  zero.

For w negative, integrate round a sector of radius R bounded by the lines  $\theta = 0$  and  $\theta = \beta$ , with  $-\tan^{-1}2\mu/\kappa_0 > \beta > -\frac{1}{2}\pi$ . We get a similar result, except that the integrand has now a simple pole within the sector at the point  $\kappa_0 - 2\mu i$  approximately. The residue at this pole gives the term in (8) which represents the regular train of waves in the rear of the system. It can also be verified that in this case y and  $\partial y/\partial w$  are finite and continuous throughout.

Returning to the general expression (6), the second integral represents the deviation from the steady state. It contains exp  $\{i\kappa(\varpi+ct)\}$  as a factor, and we see from its form that it represents the effect at time t of a certain initial distribution of velocity and displacement. To illustrate this point, consider a stationary pressure system which is suddenly established at a given instant and maintained constant. The effect is the same as if there had been in existence up to the given instant two equal and opposite systems with their ultimate static effect upon the water surface fully established, the negative system being then suddenly annulled. Thus the subsequent effect is the steady state of the positive system combined with the effect of an initial displacement equal to the steady state of an equal negative system. In the same way, for a pressure system which is suddenly established and started in uniform motion, the effect is the superposition of the steady state of this system and the disturbance due to initial conditions given by the steady state of an equal negative system in uniform motion. We shall find this principle of use in a later section.

4. The wave resistance  $R_1$  in the steady state is usually obtained from energy principles applied to the regular waves. The front of the train advances with velocity c, while the rate of flow of energy across any fixed vertical plane in the rear is the corresponding group velocity  $\frac{1}{2}c$ ; from the amplitude of the regular waves in (8), by equating the net rate of gain of fluid energy to  $R_1c$ , it follows that

$$R_1 = \kappa_0^2 \{ \phi(\kappa_0) \}^2 / g\rho. \tag{10}$$

Some consideration is necessary before we can apply this method to the motion before the steady state has been attained.

Begin with a case in which there is no ambiguity, namely, when the waves are produced by a rigid body moving horizontally through the liquid. We can apply the general hydrodynamical principle that the rate of increase of total energy of the fluid is equal to the activity of the pressure taken over all the bounding surfaces. If we equate the rate of increase of energy to the product of a force R and the velocity of the rigid body, it follows that R is simply the total fluid pressure on the moving body resolved horizontally. This result can easily be verified by direct calculation for the steady state, whether the waves are produced by the motion of a rigid body or by the motion of an assigned surface pressure; in fact, the two cases are identical in the steady state, for we can imagine the surface pressure to be applied by a rigid cover which fits the water surface everywhere.

Consider now the problem before the steady state has been established. the waves are caused by a moving rigid body, we can use either definition for the wave resistance; we can calculate it from the rate of increase of fluid energy or from the total horizontal pressure on the body. We are not discussing this case, simply because so far the analysis has proved too complicated to allow of suitable reduction. We replace this problem by that of the motion of an assigned surface pressure. Now we can calculate the rate of increase of the total energy of the fluid when the pressure system is in motion. But it would not be satisfactory to divide this quantity by the velocity of the pressure system and define the quotient as the wave resistance, for part of the increase of fluid energy is independent of the motion of the pressure system. For instance, if a stationary pressure system is suddenly established and maintained steady, the activity of the surface pressure is not zero immediately after the initial instant; there is a subsequent flow of energy, whose rate ultimately subsides to zero. From these considerations it seems that we should get results more comparable with the wave resistance of a rigid body by adopting the alternative method of calculation. follows we shall therefore calculate for any instant the total horizontal component of the surface pressure regarded as applied normally to the surface of the water; and we shall define this to be the wave resistance.

With the usual limitation that the slope of the surface is everywhere small, we have from this definition

$$R = -\int_{-\infty}^{\infty} F(w) \frac{\partial y}{\partial w} dw. \tag{11}$$

We can verify that this gives the same result (10) for the steady state. For instance, taking the expressions in (8), the part which is symmetrical with respect to the origin gives no contribution to R, and we obtain

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$$g\rho R_1 = 2 \int_{-\infty}^{0} F(\varpi) \cdot \kappa_0^2 \phi(\kappa_0) \cos \kappa_0 \varpi \, d\varpi = \kappa_0^2 \{\phi(\kappa_0)\}^2$$

or if we work directly from the integral (7), we have

$$\tau g \rho R_1 = \kappa_0 \lim_{\mu \to 0} \int_0^\infty \frac{i \kappa^3 \{\phi(\kappa)\}^2 d\kappa}{\kappa (\kappa_0 - \kappa) + \mu^3 - 2\mu \kappa i}, \qquad (12)$$

where the real part is to be taken. Under the general conditions specified for  $\phi(\kappa)$ , of, in particular, for the case given in (9), it can be shown that this leads to the same expression (10). The wave resistance in general is the sum of two parts, the steady value  $R_1$ , as given by (10), and the deviation  $R_2$ .

Using the definition (11) with the second integral in (6), we find

$$-2\pi g\rho R_{2} = \lim_{\mu \to 0} e^{-\mu ct} \int_{0}^{\infty} i\kappa^{2} V \left\{\phi(\kappa)\right\}^{2} \left[\frac{e^{-i\kappa(V-c)t}}{\kappa(V-c)-\mu ci} + \frac{e^{i\kappa(V+c)t}}{\kappa(V+c)+\mu ci}\right] d\kappa.$$
(13)

5. Consider first a special case in which the pressure system is such that there are no regular waves left in the rear, a type which Kelvin called a waveless system. It follows from (10), (12), and (13), that this is the case when the system is such that  $\phi(\kappa)$  is of the form  $(\kappa - \kappa_0) \psi(\kappa)$ , where  $\psi(\kappa)$ , remains finite. We have then

$$\int_{-\infty}^{\infty} \mathbf{F}(\mathbf{w}) \cos \kappa \mathbf{w} \, d\mathbf{w} = \phi(\kappa) = (\kappa - \kappa_0) \, \psi(\kappa). \tag{14}$$

If this system is made to travel with the velocity c, for which  $2\pi/\kappa_0$  is the free wave-length, there will be no regular train of waves in the rear. The integrals (12) and (13) now remain finite and determinate with  $\mu$  zero; we can thus simplify the expressions by making  $\mu$  zero. The integral (12) vanishes, as does also the equivalent expression (10). Then, taking the real part of (13), we find for the total wave resistance of this system at any time t

$$-\pi g \rho R = \kappa_0^{\dagger} \int_0^{\infty} \kappa \left(\kappa - \kappa_0\right) \{\psi(\kappa)\}^2 \times \{\kappa^{\dagger} \sin \kappa V t \cos \kappa c t - \kappa_0^{\dagger} \cos \kappa V t \sin \kappa c t\} d\kappa. \quad (15)$$

It is of interest to examine this solution when the integral can be evaluated exactly in finite terms. Burnside\* suggested some years ago a method of building up exact solutions of certain wave problems, and similar forms have been analysed in detail by Kelvin, after obtaining the solutions by a different method. The cases in which we can carry out the integrations in (15) lead to similar functions; we obtain them by taking

$$\psi(\kappa) = \kappa^{\frac{1}{4}} e^{-r\kappa}, \quad r > 0. \tag{16}$$

\* W. Burneide, 'Proc. Lond. Math. Soc.,' vol. 20, p. 31 (1888).

This case is the simplest of the type which allows of exact evaluation of (15), and for which the integral pressure is finite. To derive the corresponding pressure system, we make use of Euler's integrals of the form

$$\int_{0}^{\infty} \kappa^{n-1} e^{-\lambda \kappa \cos \alpha} \cos(\lambda \kappa \sin \alpha) d\kappa = \lambda^{-n} \Gamma(n) \cos n\alpha,$$

$$\lambda > 0, \qquad n > 0, \qquad -\frac{1}{2} \pi < \alpha < \frac{1}{2} \pi.$$
(17)

Using the Fourier integral theorem, combined with (16) and (17), we find

$$\pi \mathbf{F}(x) = \int_0^\infty (\kappa - \kappa_0) \kappa^{\frac{1}{4}} e^{-r\kappa} \cos \kappa x \, d\kappa$$

$$= \Gamma\left(\frac{9}{4}\right) (r^2 + x^2)^{-\frac{9}{3}} \cos\left(\frac{9}{4} \tan^{-1} x/r\right) - \kappa_0 \Gamma\left(\frac{5}{4}\right) (r^2 + x^2)^{-\frac{5}{3}} \cos\left(\frac{5}{4} \tan^{-1} x/r\right). \tag{18}$$

The two terms of this expression are easily graphed when expressed in terms of the angle  $\tan^{-1}(x/r)$ ; two numerical cases are shown later.

We can now find the resistance R for the system (18), travelling with velocity  $c = \sqrt{(g/\kappa_0)}$ . Substituting (17) in (15), and writing  $\kappa = u^2$ ,  $g^{\dagger}t = q$ , ct = p, we have

$$-\frac{1}{2}\pi y \rho R = -\kappa_0 \int_0^\infty (u^6 - \kappa_0 u^4) e^{-2ru^2} \sin p u^2 \cos q u \ du$$
$$+\kappa_0 \frac{1}{2} \int_0^\infty (u^7 - \kappa_0 u^5) e^{-2ru^2} \cos p u^2 \sin q u \ du. \tag{19}$$

The integrals involved can all be derived, by differentiation with respect to the parameters, from

$$\int_0^{\infty} e^{-(\rho-ip)u^2} \cos qu \, du = \frac{1}{2} \left[ \pi/(\rho-ip) \right]^{\frac{1}{2}} e^{-q^2/4(\rho-ip)}. \tag{20}$$

Carrying out these operations, we obtain finally

$$-\pi^{1/3}g\rho R = \kappa_0^{1/2}(4r^2 + c^2t^2)^{-5/4}e^{-gt^2r/2(4r^2 + c^2t^2)}$$

$$\times \left[\kappa_0^{\frac{1}{2}}\left\{-\frac{1}{8}A\sin\left(\frac{7}{2}\theta - \phi\right) + \frac{4}{16}q^2A^2\sin\left(\frac{9}{2}\theta - \phi\right) - \frac{1}{3}\frac{5}{2}q^4A^3\sin\left(\frac{1}{2}\theta - \phi\right) + \frac{4}{16}q^6A^4\sin\left(\frac{7}{2}\theta - \phi\right) + \kappa_0^{3/2}\left\{\frac{3}{4}\sin\left(\frac{5}{3}\theta - \phi\right) - \frac{3}{4}q^2A\sin\left(\frac{7}{4}\theta - \phi\right) + \frac{1}{16}q^4A^2\sin\left(\frac{9}{4}\theta - \phi\right)\right\} + \frac{1}{16}q^6q^4A^2\cos\left(\frac{9}{2}\theta - \phi\right) - \frac{1}{3}\frac{0}{2}q^2A^3\cos\left(\frac{1}{2}\theta - \phi\right) + \frac{2}{16}\frac{1}{4}q^5A^4\cos\left(\frac{1}{3}\theta + \phi\right) - \frac{1}{12}q^7A^5\cos\left(\frac{1}{3}\theta - \phi\right) + \frac{2}{16}\frac{1}{4}q^5A^4\cos\left(\frac{1}{3}\theta + \phi\right) - \frac{1}{12}q^7A^5\cos\left(\frac{1}{2}\theta - \phi\right) + \kappa_0\left\{-\frac{1}{6}qA\cos\left(\frac{7}{2}\theta - \phi\right) + \frac{5}{8}q^3A^2\cos\left(\frac{9}{2}\theta - \phi\right) - \frac{1}{3}\frac{1}{4}q^5A^3\cos\left(\frac{1}{4}\theta - \phi\right)\right\}\right\},$$
(21)

where

$$q = g^{\dagger}t$$
;  $\Lambda = (4r^2 + c^2t^2)^{-\frac{1}{2}}$ ;  $\theta = \tan^{-1}(ct/2r)$ ;  $\phi = gct^2/4(4r^2 + c^2t^2)$ .

6. Before working out numerical examples, it is convenient to record the asymptotic expansion suitable for large values of ct/2r. From (21), by

writing  $\theta = \frac{1}{2}\pi - \tan^{-1}(2r/ct)$ , and expanding the various terms, we get, up to and including terms in  $(2r/ct)^{3/2}$ ,

$$-\pi^{1/2}g\rho R = \frac{3}{12\pi}g^4e^{-17/2}t^{-1/2}e^{-\beta}\cos\left(gt/4c + \frac{1}{4}\pi\right) + \frac{3}{14\pi}g^2e^{-16/2}t^{-3/2}\left(37 + \beta\left(18\beta - 75\right)\right)e^{-\beta}\cos\left(gt/4c - \frac{1}{4}\pi\right), \quad (22)$$

where  $\lambda_0 = 2\pi c^2/g$  and  $\beta = \pi r/\lambda_0$ . If the pressure system has moved through n wave-lengths, we have  $ct = n\lambda_0$ , and the ratio of the amplitudes of the two terms in (22) is

$$\frac{1}{9\pi n} \left\{ 37 + \frac{\pi r}{\lambda_0} \left( \frac{18\pi r}{\lambda_0} - 75 \right) \right\}, \qquad (23)$$

an expression which gives some estimate of the approximation obtained by using only the first term of (22). It depends not only upon the distance travelled, but also upon the ratio of the effective breadth of the system to the free wave-length for the assigned velocity.

Compare this approximation with that obtained by applying Kelvin's group method directly to the integral expression for the wave resistance.

Under certain conditions,\* an approximate value of an integral of the form

$$\cdot \int_a^b \mathbf{F}(\kappa) e^{if(\kappa)} d\kappa$$

is given by

$$\frac{\sqrt{\pi \operatorname{F}(\alpha)}}{\sqrt{\left|\frac{1}{2}f''(\alpha)\right|}}e^{i\{f(\alpha)\pm\pi/4\}},\tag{24}$$

the upper or lower sign being taken in the exponential according as  $f''(\alpha)$  is positive or negative, and  $\alpha$  being a root of  $f'(\alpha) = 0$ . It is assumed that the circular function in the integral goes through a large number of periods within the range of integration, while  $F(\kappa)$  changes comparatively slowly; in addition, the quotient  $f'''(\alpha)/\{f''(\alpha)\}^{3/2}$  must be small.

Apply this to the form for F given in (13). The second term within the square brackets contributes nothing to the approximation; from the first term we have, with  $ct = n\lambda_0$ ,

$$f(\kappa) = -\kappa (V - c) t = -g^{\frac{1}{6}} t \kappa^{\frac{1}{6}} + ct \kappa.$$

Hence

$$\alpha = g/4c^2$$
;  $f''(\alpha) = 2c^3t/g$ ;  $f'''(\alpha)/\{f''(\alpha)\}^{3/2} = 3/\sqrt{(\pi n)}$ .

From (13) and (24) the group value of R is

$$R = -\frac{1}{2\pi g\rho} \lim_{\mu \to 0} e^{-\mu ct} \sqrt{\left(\frac{\pi g}{c^3 t}\right)} \frac{ig^{1/2} \alpha^{3/2} \{\phi(\alpha)\}^2}{g^{1/2} \alpha^{1/2} - c\alpha - i\mu c} e^{i(gt/4c - \pi/4)}.$$
 (25)

Taking the real part of this expression and putting  $\mu$  zero, we obtain

$$R = -\frac{g^{1/2} \{\phi (g/4c^2)\}^2}{4\pi^{1/2} \rho c^{7/2} t^{1/2}} \cos (gt/4c + \frac{1}{4}\pi).$$
 (26)

\* Lamb, 'Hydrodynamics,' p. 385.

It should be noted that for a pressure system which leaves regular waves in its rear, we cannot take (26) as an approximation for the limiting value of (13) when  $\mu \to 0$ , except under certain further limitations. For the present this difficulty does not arise, as we are considering a waveless system with  $\phi$  ( $\kappa$ ) of the form ( $\kappa - \kappa_0$ )  $\psi(\kappa)$ ; we have seen that in this case the integrals (12) and (13) remain finite and determinate with  $\mu$  zero.

In particular, for the forms (16) and (18), the group formula (26) reduces to

$$-\pi^{1/2}g\rho R = \frac{9}{19R}g^4c^{-17/2}t^{-1/2}e^{-\pi\tau/\lambda_0}\cos(gt/4c + \frac{1}{4}\pi), \tag{27}$$

which, from (22), agrees with the first term in the asymptotic expansion of the exact solution for this case.

Instead of expressing R as a function of the time t, we can use the distance travelled, or again the number n of free wave-lengths  $\lambda_0$  through which the system has moved; in the last case the circular function in (27) becomes  $\cos \frac{1}{2}(2n+1)\pi$ . The form of (27) agrees with the definition of the wave resistance as the resolved total pressure. For after a sufficient time, the surface in the neighbourhood of the moving origin consists chiefly of the simple waves whose group velocity is the velocity c of the pressure system; thus the wave-length there is  $4\lambda_0$ .

7. Consider now two numerical examples of the exact solution (21) with different values of the ratio  $r/\lambda_0$ .

In the first place, we shall adopt units used by Kelvin, for comparison and for simplicity of calculation.

Case i: 
$$y = 4$$
;  $r = 1$ ;  $\lambda_0 = 2$ ;  $\kappa_0 = \pi$ ;  $c = 2/\sqrt{\pi}$ .

From (18) the pressure system F(x) can be obtained by graphing

$$4\pi \cos^{5/4}\theta \cos \Phi - 5 \cos^{9/4}\theta \cos \Phi \theta$$

where  $\theta = \tan^{-1}(x/r)$ . The graph is shown in curve (1) of fig. 1; the curve has maxima near  $x = \pm 0.2$ , though they are almost inappreciable on the diagram.

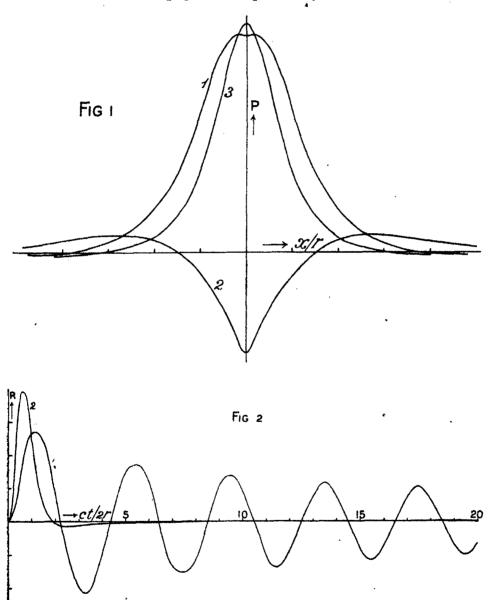
It is convenient to graph the resistance curve upon a base  $\xi = ct/2\tau$ ; in this particular case  $\xi$  is also the number of wave-lengths  $\lambda_0$  through which the system has moved. The angles of the formula (21) are now

$$\theta = \tan^{-1}\xi; \quad \phi = \pi \xi^3/2(1+\xi^2).$$

It is unnecessary to repeat the expression (21) with these values; each of the 14 terms can be easily calculated for any given value of  $\xi$ . The results are shown in curve (1) of fig. 2; to obtain the curve 15 points were calculated by the formula (21).

The wave resistance decreases ultimately to zero, as it should for a waveless

system, but it approaches the steady state very slowly. This is explained when we examine the graph of the pressure system in this case. The



waveless character is due to the mutual interference effects produced by the peaks of the pressure graph, and fig. 1 shows how inappreciable the peak

are in this case. Hence the slowness with which the steady state is attained and the probable lack of stability of the steady state.

To compare the group approximation with the exact solution, we have from (27)

$$-\pi^{1/2}g\rho R = 9 \times 2^{-15/2}\pi^4 n^{-1/2}e^{-\pi/2}\cos\frac{1}{2}(2n+1)\pi.$$
 (28)

The following is a comparison of the values of  $10^2\pi^4g\rho$ R, as given by (28) and the exact formula (21):

n.	Group.	Exact.		
9	-28 .73	-26 ·45		
16	+ 17 .77	+16 04		
25	-14.21	-14 93		
100	+ 7.11	+ 6 94		

Case ii.—As a second numerical example, we take one which might correspond more to practical conditions, in that the pressure system is similar to that associated with the motion of a ship model in an experimental tank. Using foot-second units, we take

$$y = 32$$
;  $r = 2$ ;  $c = 20$ ;  $\kappa_0 = 0.08$ ;  $\lambda_0 = 25\pi$ .

The pressure system is graphed in curve (2) of fig. 1, from the expression  $8\cos^{5/4}\theta\cos\frac{5}{4}\theta-125\cos^{9/4}\theta\cos\frac{9}{4}\theta$ . We notice the contrast between this and the previous case. We should now expect the steady state to be attained quickly and to be much more stable. This is brought out very clearly by the resistance curve, which has been graphed from (21), and is shown in curve (2) of fig. 2; after the initial peak, the subsequent oscillations can scarcely be shown on the scale of the diagram.

A comparison of the exact formula and the group approximation gives similar results to the previous case, for in both the numerical value of the ratio (23) is of the order 1/n, in spite of the difference in the values of  $r/\lambda_0$  for the two cases.

It should be remarked that the two cases cannot be compared as regards absolute values from the curves shown, because the scale for the ordinates has been chosen arbitrarily in each case. The maximum value of R, that is, the value at the prominent peak on curve (2), is given by  $g\rho R = 7 \times 10^{-8}$ . We can obtain some idea of the magnitude by the following comparison: We have chosen the pressure system so that it is waveless at a particular velocity, namely, 20 feet per second. Now, imagine the same system to be

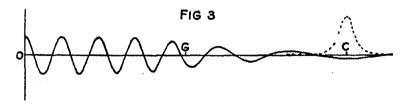
driven at any other steady velocity; it will have a steady resistance, which we can calculate from the formula (10); in this case it is

$$g\rho R = \kappa^{5/2} (\kappa - 0.08)^2 e^{-4\kappa}, \qquad \kappa = g/V^2.$$
 (29)

This steady wave resistance has a maximum at a velocity of about 5.25 ft./sec., and the value of  $g\rho R$  is then  $16.4 \times 10^{-3}$ . Hence the maximum resistance due to the sudden starting of the system at its waveless speed is about one-half the maximum steady resistance at any uniform speed.

8. We have been able to obtain an exact solution for a special type of waveless system; we leave this now to consider more generally a symmetrical localised pressure system, which is suddenly established and set in motion.

We have seen that the surface elevation at any time is found by superposing the steady state of the system and the effect due to initial conditions given by the steady state of an equal negative system in uniform motion. Apply this to a case in which the steady state consists of an infinite train of regular waves in rear of the system, together with a localised displacement symmetrical with respect to the moving origin. Let O be the fixed origin and starting point, and C the position at time t. The deviation from the ultimate steady state consists of the effect due to a certain initial distribution of displacement and velocity localised round O, together with the subsequent state of a semi-infinite train of regular waves, which at the initial instant had a definite front at the point O. We may describe the latter part in general terms as a regular train with a front, more or less definite according to the time, at a point G corresponding to the group velocity, and in advance of G a disturbance which may be called the forerunner. If OC is sufficiently large, and if we require the surface elevation only at points sufficiently far in advance of G, the forerunner is given with considerable accuracy by Kelvin's group method of approximation. The argument is represented diagrammatically in fig. 3, the continuous line showing the elevation and the dotted line the travelling pressure system.



The wave resistance being defined as the total horizontal component of the pressure system, we divide it into two parts. The first part is the final steady value  $\kappa_0^2 \{\phi(\kappa_0)\}^2/g\rho$  as given in (10), and the second is the deviation given by the integral in (13). The latter represents the resolved pressure

system as if the surface elevation were that due to the stoppage of a negative system, as represented in fig. 3.

For a concentrated pressure system, the value of the integral (13) will be given approximately by the Kelvin group method, if the time is sufficiently large; that is, if C is sufficiently far in advance of G for us to neglect the contribution of the applied pressure acting on the surface to the rear of G.

Without attempting to specify these conditions more precisely, we shall apply the method to the type of system used in the previous sections; from the previous exact solution we have been able to estimate somewhat the degree of accuracy of the group approximation.

The group value of (13) is given in (26). Hence the wave resistance, for sufficiently large values of t, is given by

$$R! = \frac{g}{\rho c^4} \left\{ \phi \left( \frac{g}{c^2} \right) \right\}^2 - \frac{g^{1/2} \left\{ \phi \left( g/4c^2 \right) \right\}^2}{4\pi^{1/2} \rho c^{7/2} t^{1/2}} \cos \left( gt/4c + \frac{1}{4}\pi \right). \tag{30}$$

9. Apply this to the pressure distribution

$$\pi F(x) = \Gamma(\frac{9}{4})(r^2 + x^2)^{-9/8} \cos{\{\frac{9}{4}\tan^{-1}(x/r)\}},$$
 (31)

for which  $\phi(\kappa) = \kappa^{5/4}e^{-r\kappa}$ , with  $\kappa = g/c^2$ . The graph of this distribution is shown in curve (3) of fig. 1.

We have

$$\rho R = \frac{g^{7/2}}{c^9} e^{-2g\tau/c^4} - \frac{g^3}{128\pi^{1/2}c^{17/2}t^{1/2}} e^{-g\tau/2c^4} \cos(gt/4c + \frac{1}{4}\pi).$$
 (32)

The value of R oscillates about the final steady value. The relative deviation is given by the ratio of the two terms, namely,

$$2^{-15/2}\pi^{-1}n^{-1/2}e^{3\pi r/\lambda_0}\cos\frac{1}{2}(2n+1)\pi$$

where  $\lambda_0$  is the wave-length of the regular train and  $ct = \lambda n_0$ . We may obtain numerical values by using the two cases of the previous sections.

For Case i we have r=1,  $\lambda_0=2$ , and we find the following comparison between  $R_1$ , the final steady resistance, and  $R_2$ , the deviation given by the second term of (32):—

n.	$\mathbf{R_2/R_1}$ .
9	+0.046
16	-0 °085
25	+0.027
100	~0.014

Hence, after the system has moved through nine wave-lengths, the deviation is less than 5 per cent.

In Case ii, r=2 and  $\lambda_0=25\pi$ . We find that when n=9, the deviation is already less than 0.06 per cent.

10. Consider now a simpler type of localised pressure distribution, namely,

$$\pi F(x) = r/(r^2 + x^2). \tag{33}$$

This type leads to a steady wave resistance whose variation with the velocity is more like that of a ship model. We have  $\phi(\kappa) = e^{-r\kappa}$ , and (30) gives

$$\rho R = \frac{g}{c^4} e^{-2g\tau/c^3} - \frac{g^{1/2}}{4\pi^{1/2} c^{7/2} t^{1/2}} e^{-g\tau/2c^3} \cos(gt/4c + \frac{1}{4}\pi).$$
 (34)

The relative deviation is now 32 times as large as in the previous case, since

$$\frac{R_2}{R_1} = \frac{e^{3\pi r/\lambda_0}}{2^{5/2}\pi n^{1/2}} \cos \frac{1}{4}(2n+1)\pi.$$

With r = 1,  $\lambda_0 = 2$ , the value of  $R_2/R_1$  is about 0.5 for n = 100. We should have to take n of the order 10,000 before bringing the deviation from the steady value below 5 per cent.

On the other hand, with  $r=2, \lambda_0=25\pi$ , the deviation is under 2 per cent. when n = 9, or at about 35 seconds after the beginning of the motion; it is less than 2 per cent, when n=4, or after a travel of rather more than 300 feet.

11. The waves produced by the horizontal motion of a circular cylinder of small radius travelling at a considerable depth h below the surface may be compared with those produced by the surface pressure

$$\pi F(x) = Ac^2 (h^2 - x^2)/(h^2 + x^2)^2.$$
 (35)

We assume that the intensity of the system is proportional to the square of the velocity. It appears that the steady wave resistance is then the same function of the velocity as in the motion of the cylinder;\* for we have

$$\phi(\kappa) = Ac^2\kappa e^{-\kappa h},$$

and hence

$$\rho R = \frac{A^2 g^3}{c^4} e^{-2gh/c^2} - \frac{A^2 g^{5/2}}{64 \pi^{1/2} c^{7/2} t^{1/2}} e^{-gh/2c^2} \cos(gt/4c + \frac{1}{4}\pi).$$
 (36)

As a numerical example, take the case when the velocity is such that the steady resistance  $R_1$  has its maximum value; that is, when  $c^2 = gh$ . Then we have

$$\frac{R_2}{R_1} = \frac{e^{3/2}}{2^{13/2}\pi n^{1/2}}\cos\frac{1}{4}(2n+1)\pi. \tag{37}$$

The value of the ratio means a deviation from the steady value of about 0.8 per cent. when  $n=3\frac{1}{2}$ , that is, when the system has travelled through a distance  $7\pi h$ .

<sup>\*</sup> Lamb, 'Hydrodynamics,' p. 408.

# Spectroscopic Observations on the Active.Modification of Nitrogen.—V.\*

By the Hon. R. J. STRUTT, F.R.S.

(Received January 3, 1917.)

[PLATE 1.]

## § 1. Introduction.

The spectrum of the nitrogen afterglow, as ordinarily obtained,† consists of three groups of bands, which we designated as the  $\alpha$ ,  $\beta$ , and  $\gamma$  groups. The  $\alpha$ -group is in the visual region, and consists of a selection of the first positive bands of nitrogen. The  $\beta$ -group is chiefly in the ultra-violet, but extends into the violet. It can be observed in the discharge, but is much better developed in the afterglow. The  $\gamma$ -group is wholly in the ultra-violet, and identical with Deslandres' third positive nitrogen group.

I have not much to add to the results of the former paper as regards the measurement and classification of these various groups of bands. The circumstances under which they appear have, however, been reinvestigated, and the conclusions of the earlier paper modified in some important respects.

## § 2. a-Group of Bands.

In the earlier investigation it was found that the intensity of four groups of bands of the first positive group was extraordinarily enhanced as compared with their ordinary intensity in the discharge. The remaining bands came out only faintly, though some of them are quite perceptible in the photograph reproduced (p. 388), particularly 6394:45, 6468:53, 6544:81, and 6623:52.

There was some doubt whether these faint bands really form part of the afterglow spectrum at all. There are two causes of uncertainty. First, it is not easy, without special precautions, to be certain of avoiding stray electric discharges in the afterglow chamber, which might bring in these faint bands. Secondly, though the light of the generating discharge cannot enter the spectroscope slit directly, a part of it may enter by stray reflection from the inside glass walls of the apparatus.

As the presence or complete absence of these bands in the true afterglow

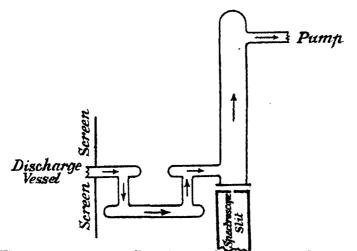
<sup>\*</sup> I, 'Roy. Soc. Proc.,' A, vol. 85, p. 377 (1911); II, ibid., vol. 86, p. 105 (1911); III, ibid., vol. 89, p. 187 (1913); IV, ibid., vol. 91, p. 120 (1915).

<sup>†</sup> See Fowler and Strutt, 'Roy. Soc. Proc.,' A, vol. 85, p. 189, and earlier literature then cited.

spectrum seems likely to be an important point, when the subject becomes ripe for theoretical treatment, special experiments have been made to attain certainty. To secure perfect freedom from electric discharges in the observation tube, the discharge tube, with induction coil, jar, and spark-gap, were all enclosed in an earthed metal box, the observation tube being outside. Other additional precautions were taken as described previously.\* These measures were quite successful. There was no tendency to stray discharge in the observation tube. The tests applied to prove this will be mentioned later.

The faint group of bands in the region of  $\lambda$  6500 still remained, without perceptible diminution of intensity. They were therefore certainly not to be attributed to the light of stray discharges in the observation vessel.

To test whether they were due to stray light from the generating discharge, all light-passing through the glass walls of the discharge vessel was cut off by suitable screens. The glowing gas was passed from the discharge vessel to the observation vessel by a cranked glass tube, with four rectangular bends constructed as shown (fig. 1), so as to minimise internal reflection. The cranked tube was wound over with a strip of opaque black cloth (not shown). The electrical screening precautions were still used.



The arrows indicate direction of the stream of glowing gas.

F16. 1.

Under these conditions, the bands in the region  $\lambda$  6500 were still visible, and their intensity relative to the main bright bands of the afterglow spectrum was not less than when the cranked tube was dispensed with,

<sup>\* &#</sup>x27;Roy. Soc. Proc.,' A, vol. 87, p. 183 (1912).

though the latter must have diminished stray light from the discharge many times. It is clear that these bands truly form part of the afterglow spectrum.

# § 3. The \( \beta \) and \( \gamma \) Groups in the Afterglow.

These groups are quite distinct from one another in their numerical relations, but in the afterglow, in most cases, though not in all, they appear together in a nearly constant relative intensity. It is true that if the spectrum is faint, some of the more intense  $\beta$ -bands come out in the absence of the  $\gamma$ -group, but this is only a photographic phenomenon, and not a true separation of the two groups.

After the investigations on the action of catalysts in production of active nitrogen,\* it appeared desirable to re-examine the question of the origin of the  $\beta$  and  $\gamma$  groups. For the view had been expressed that these groups were both due, in some way, to oxides of nitrogen.† I had come to the conclusion (loc. cit.) that a bright visual afterglow ( $\alpha$ -group of bands) always required the presence of traces of some other substance with the nitrogen in the discharge. Starting with pure nitrogen, we may enhance the  $\alpha$ -group of bands by introducing traces of oxygen, or some substance such as carbon dioxide which will yield oxygen by decomposition in the discharge; or we may enhance them by introducing traces of hydrocarbons, or hydrogen sulphide, which do not yield oxygen.

It was found that those admixtures which do yield oxygen brightened up the  $\beta$  and  $\gamma$  groups along with the visual afterglow ( $\alpha$ -group); while the other class of admixtures brightened up the visual afterglow without brightening up the  $\beta$  and  $\gamma$  groups.

In carrying out these experiments, the same methods have been used as were employed in determining the action of the various catalysts. The nitrogen was purified by prolonged heating with sodium at  $300^{\circ}$  C., so that it gave practically no afterglow. The various small admixtures were fed in through a capillary tube to the amount of about  $\frac{1}{800}$  part. The spectra were photographed under precisely comparable conditions before and after adding the admixture.

These experiments clearly showed that the  $\beta$  and  $\gamma$  groups of bands are not essentially bound up with the  $\alpha$ -group; their intensity relative to the latter is greater when a substance capable of yielding oxygen is present in the nitrogen before it passes through the discharge.

If therefore nitrogen prepared in any particular way shows these bands in the afterglow, there is reason to infer the presence of oxygen compounds in

<sup>\* &#</sup>x27;Roy. Soc. Proc.,' A, vol. 91, p. 303 (1915).

<sup>+</sup> E. P. Lewis, 'Phil. Mag.,' June, 1913.

I had already come to the conclusion that nitrogen prepared by the method which I have generally used, namely, prolonged standing over moist phosphorus, and drying with phosphorus pentoxide, must be admitted to contain carbon dioxide. With the ready spectroscopic test for oxygen compounds, I studied to eliminate them from the gas thus produced. It was found that the B and y bands persisted in the phosphorus nitrogen when bubbled through very strong alkali, containing pyrogallol, previous to drying. Attention was then turned to the adequacy of the drying, and it was found that the large tube of phosphorus pentoxide employed, measuring  $35 \times 4$  cm., was insufficient. Additional drying tubes diminished the intensity of the  $\beta$  and  $\gamma$  bands, until, with many long tightly packed tubes containing about 1.5 kgrm. of phosphorus pentoxide altogether, the B and y groups were very inconspicuous on the photographs unless long exposure was given.

Although the  $\beta$  and  $\gamma$  groups had been got rid of, it was now found that the violet cyanogen groups of bands were fairly strong. No doubt the carbon contamination responsible for them had been present before, but the B and y bands had in some way monopolised the energy available for excitation. To reduce the cyanogen bands the apparatus was modified. All indiarubber was dispensed with; glass stoppers, cemented in with sealingwax, were used on the gas holders, and all other joints were fused together. The phosphorus was placed in a perforated zinc bucket instead of a muslin The gas was bubbled through a column of strong sulphuric acid bag. 10 inches deep, and was then passed through a tube of soda lime 3 cm. diameter and 1 metre long to the phosphorus pentoxide tubes. The rate of flow was 9 litres per hour, and was controlled by a tightly rammed plug of phosphorus pentoxide at the end of the drying tubes, which was found in practice to keep the flow into a vacuum very constant from day to day over many weeks.

Under these conditions, with new freshly cut phosphorus, the cyanogen spectrum was strong at first, but after a few refillings of the gas holder (it was refilled daily and allowed to stand overnight), the cyanogen bands became less conspicuous. They were never got rid of, and the carbon is, no doubt, contained in the phosphorus itself. In setting up a fresh apparatus, I should attempt to remove it by means of chromic acid.

Plate 1, No. 1, shows the spectrum of the afterglow from gas thus treated. The plates used were not sensitive to green or yellow, thus the a-bands (visual afterglow) are not seen on this or any of the succeeding photographs. The strongest line in the spectrum, strangely enough, is the mercury line at 2536. There was no mercury visibly present in the

apparatus or in the Gaede molecular pump used with it. A small mercury pressure gauge had, indeed, been previously connected to it, but this had been removed, and large volumes of nitrogen (perhaps 50 litres) passed through the system of tubes before the photograph was taken. The sensitiveness of this test for mercury seems to be extraordinary. Besides the mercury line the strongest cyanogen band at 3883 is fairly conspicuous, and several of the stronger bands of the  $\beta$ -group are faintly seen. The aggregate intensity of these latter, faint though they are, perhaps entitles them still to be considered the most important feature of this spectrum, outside the visual region.

It is believed that further drying would be needed to eliminate the  $\beta$  and  $\gamma$  groups entirely; but the system of drying tubes could hardly be increased to any considerable multiple of its present dimensions, already formidable. I have never succeeded in purifying a sample of nitrogen that had been freed from oxygen in the wet way to the point where the visual yellow afterglow ( $\alpha$ -bands) fails, nor so far as I know has anyone else done so. For this it is still necessary to have recourse to heated sodium or some such method. But the phosphorus nitrogen, purified as described, has served well for investigating the origin of the  $\beta$  and  $\gamma$  groups.

# § 4. Controlled Development of $\beta$ and $\gamma$ Bands.

Having thus at disposal a ready means of preparing nitrogen which gave the  $\beta$  and  $\gamma$  groups very faintly, I proceeded to observe the effects of introducing various oxygen-containing gases into the afterglow, after the gas had passed through the discharge tube and not sooner. The observations made, though quite sharp and distinct, are at present very difficult to co-ordinate fully.

In general, the effect of introducing oxygen or its compounds into the afterglow is to develop the  $\beta$  and  $\gamma$  groups of bands. In some cases this development is very strong; in no case have I seen it produced by introduction of gases which do not contain oxygen. Some of the admixtures produce special phenomena requiring description, and these will be detailed in the form of a catalogue.

For the admission of the gases, it was found convenient to use a screw-down gunmetal stopcock (one of those supplied as a fine adjustment valve for oxygen cylinders), drawing the gas towards the point of the regulating cone, so as not to put suction on to the gland. Such a valve admits of far more definite and stable regulation than a glass stopcock, with the necessary semi-fluid lubricant. The rate of admission was measured by a capillary tube with a manometer connected across its ends. The flow of nitrogen was in all cases

9 litres per hour. The amount of other gas fed into it after it had left the discharge tube will be stated in connection with each experiment.

Oxygen.—From earlier observations\* it was believed that oxygen merely destroyed the  $\alpha$ -group luminosity, without the substitution of any other spectrum. This belief is now recognised to have been mistaken. The spectrum generated escaped observation partly because it was already initially present owing to impurities in the nitrogen used, but mainly because it is situated almost entirely in the ultra-violet, and is therefore difficult to recognise visually.

Oxygen, or more conveniently air, gives, in fact, the  $\beta$  and  $\gamma$  groups when introduced into the afterglow. Spectrum No. 2, Plate 1, shows this. The spectra Nos. 1 and 2 are strictly comparable, being taken on the same plate, and with the same exposure, all adjustments undisturbed, except that for No. 2 air was admitted to the afterglow at 570 c.c. per hour, the nitrogen flow being as usual, 9 litres per hour. The positions of the strongest  $\beta$  and  $\gamma$  bands are indicated in the strips below the series of photographed spectra. It will be seen how enormously these groups, barely visible before, are now enhanced.

It was important to make sure that stray discharges were not occurring through the mixed gases in the observation vessel, since these would give rise to oxides of nitrogen. The greatest care was taken to make sure of this by working at a fairly high pressure (1 cm. of mercury) and by connecting to earth the electrode of the discharge tube nearest the observation tube. The test of success is for the observer to place his hand on the observation tube, and at the same time to watch the luminous effects, preferably through a blue glass. If stray discharge is present, the luminosity will, without fail, be seen to move, owing to changed distribution of electrostatic capacity. The blue glass gives an advantage, since stray discharges, if present, yield much more blue light than does the nitrogen afterglow.

Further, if stray discharge were present, it would bring in the second positive series of bands. These, however, were absent from the photographed spectra.

It was also important to establish that the appearance of the  $\beta$  and  $\gamma$  bands in these experiments was not conditioned by diffusion of oxygen back into the discharge tube against the gas stream. Photograph No. 9, Plate 1, shows a tube through which active nitrogen is flowing. It was taken on a colour-sensitive plate through a yellow screen, which cut off all blue light, and, therefore, transmitted the  $\alpha$ -group of bands only. Air was flowing in through the side entrance indicated, but, as will be observed, its entry does

<sup>\* &#</sup>x27;Roy. Soc. Proc.,' A, vol. 85, p. 224 (1911).

not produce any sudden change in the luminous effects. This photograph fairly represents the visual appearance. Introduction of air makes the yellow glow die away more quickly but does not introduce any sudden or obvious change in its visual character.

Photograph No. 10 (Plate 1) was taken under exactly the same conditions as No. 9, except that a blue uviol glass screen was substituted for the yellow screen, also an ordinary plate for the colour-sensitive one. The actinic effect is now mainly due to the  $\beta$ -group (the  $\gamma$ -group hardly penetrates glass lenses) and it is very clear that this spectrum originates at the place where the air tributary enters, extending only downstream.

Visual examination through blue glass shows these effects as clearly as the photograph does. The last members of the  $\beta$ -group, at wave-lengths 4029, 4297, 4590, 4930,\* though of small intensity, are within the visual region, and can be observed if the visually strong  $\alpha$ -group is cut out with a blue glass. It is necessary, however, to have the nitrogen used as free as possible from hydrocarbon contamination; for if the violet cyanogen group is strongly present, it will be quenched by admission of air, and the result will be to diminish rather than increase the light seen through a blue glass.

It is also possible to recognise the bluish tinge of the afterglow caused by the introduction of air, even without a blue glass, but this is only seen some distance downstream, when the  $\alpha$ -group intensity has diminished considerably. The effect is not very conspicuous unless specially looked for, and escape notice in the earlier observations, where much more striking phenomena were being discovered daily.

Comparative spectrograms were taken, each with 5 minutes' exposure, with increasing admissions of air, maintaining the nitrogen flow and the discharge conditions constant. The afterglow tube was presented end-on to the slit, and it was long enough for the glow to die away to a comparatively small intensity before the gas emerged. It was found that, under the experimental conditions, the maximum effect was obtained with admission of about 70 c.c. of air per hour. Increasing the admission did not produce much effect on the photographic intensity until more than 570 c.e. was admitted. After this, the  $\beta$  and  $\gamma$  intensities were diminished. There was, however, no distinct variation in the relative intensities of these two groups throughout the experiments with air.

Carbon Dioxide.—This gas, like oxygen, brings in the  $\beta$  and  $\gamma$  groups very strongly. See No. 3, Plate 1, which was taken with an influx of 1100 c.c. of carbon dioxide per hour, with the nitrogen flow and other conditions as before. It will be noticed by a careful comparison of Nos. 2 and 3 that the  $\beta$ -group

<sup>\*</sup> These two latter were not included in the earlier description of the spectra.

is stronger relative to the  $\gamma$ -group with carbon dioxide than with air. All the numerous photographs taken at different times with carbon dioxide consistently show the same effect, so as to leave no doubt of its being definitely characteristic of this gas.

The blue glow caused by introduction of carbon dioxide into the afterglow can be detected visually by the same methods as with air.

The maximum effect was reached by admitting 570 c.c. of carbon dioxide per hour, but much larger quantities could be added without diminishing the  $\beta$  and  $\gamma$  intensity again. The largest admission tried was 2280 c.c. per hour, which still gave about the same effect.

Carbon Monoxide (see Plate 1, No. 4).—This gas gave complex effects, requiring careful description.

In the first place, it gave a visual spectrum with bands in the green, which, as obtained hitherto, is too faint for satisfactory study, and has not been identified. A more resolute attack on this problem would be desirable, but attention has been claimed by other questions which seemed more urgent.

Secondly, the violet bands of cyanogen were excited, so that the small intensity of these bands already present, and due to impurity in the nitrogen, was notably increased. It is difficult to be absolutely certain that the strengthening of these bands is not due to impurity in the carbon monoxide, for a very small quantity of any hydrocarbon brings them in strongly. But the cyanogen-intensity did not seem to vary appreciably whether the carbon moxoxide was prepared from oxalic or from formic acid. Again, I litre of the gas from formic acid was liquefied by liquid air boiling under reduced pressure, and allowed to distil away fractionally into the observation tube; but I was unable to detect any variation in the cyanogen-intensity during the course of the distillation, which was continued till the stock of liquid carbon monoxide was exhausted.

No formation of cyanogen compounds was chemically detectable. The mixed gases from the observation tube were led through a cooled tube, which was subsequently washed with caustic potash solution, but no cyanide could be detected in the latter; though, if a hydrocarbon had been substituted for carbon monoxide, the Prussian blue reaction would have been very strong.

But, to return to the spectra associated with carbon monoxide, there was, thirdly, the  $\gamma$ -group strong, with the  $\beta$ -group relatively very weak. This effect is quite exceptional and peculiar to carbon monoxide.

Comparative photographs were taken as before, each with 5 minutes' exposure, and increasing influx of carbon monoxide. The \$\beta\$-group and the

cyanogen group were about at their maximum over a range of 140 to 570 c.c. per hour, the  $\gamma$ -group from 280 to upwards of 2200 c.c. per hour. It is therefore with large admissions that the great relative intensity of the  $\gamma$ -group is most conspicuous. This suggests that excess of carbon monoxide above what is required for developing the spectra in some way damps out the  $\beta$ -group, without damping out the  $\gamma$ -group to the same extent.

The photograph reproduced (Plate 1, No. 4) was taken with admission of 1140 c.c. of carbon monoxide per hour.

It was of interest to try whether a mixture of ethylene and air, which, like carbon monoxide, would give the  $\beta$  and  $\gamma$  groups along with the violet cyanogen bands, would show the same weakness of the  $\beta$  relative to the  $\gamma$  group. Various mixtures were admitted at various rates, but nothing of the kind was observed (see Plate 1, No. 5). This photograph was taken with admission of 70 c.c. per hour of a mixture of one part ethylene to five parts air.

Nitric Oxide.—The effects of this gas also are complicated. They have been partly described in earlier communications, but there are some corrections to be made, and it will be convenient to begin afresh.

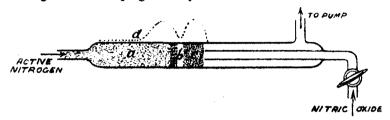
Small quantities of nitric oxide bring in the  $\beta$  and  $\gamma$  groups, the relative intensities are the same as with oxygen, and the maximum intensity obtainable is also about the same, but a smaller amount of nitric oxide will develop it (see Plate 1, No. 6). The influx ranged from 21 to 53 c.c. per hour for maximum intensity. A larger amount of nitric oxide diminishes the intensity of the  $\beta$  and  $\gamma$  groups.

Development of the  $\beta$  and  $\gamma$  groups by nitric oxide is accompanied by a marked quenching of the  $\alpha$ -group, so that the blue colour is conspicuous under suitable conditions, even without the help of a blue glass. This effect is much more marked with nitric oxide than with air.

When the nitric oxide influx is increased enough to diminish the intensity of the  $\beta$  and  $\gamma$  groups considerably, a sudden and apparently discontinuous change comes over the spectrum. This occurred under the actual conditions at 200 c.c. nitric oxide per hour. The  $\beta$  and  $\gamma$  groups disappear, and a continuous spectrum, visually of characteristic greenish-yellow colour, is substituted (see Plate 1, No. 8). This continuous spectrum will be seen to extend to about 4300 on the violet side. Its extent on the other side is determined by the limit of plate sensitiveness.

The experiment of fig. 2 illustrates further this very peculiar behaviour of nitric oxide. The tube is arranged so that the nitric oxide supply can diffuse back a short distance against the oncoming stream of active nitrogen. At the same time, by supplying the nitric oxide through a concentric inside

tube, lateral disturbance is avoided, and the flow is nearly one-dimensional. Proceeding from left to right, the concentration of nitric oxide relative to active nitrogen increases progressively.



F1g. 2.

If the tube is viewed without any coloured screen, the region a is seen filled with orange glow, due to the  $\alpha$ -group of bands, but at the right of this region the orange glow fades off, and is replaced by a fringe of violet. This is due to the less refrangible members of the  $\beta$ -group, and is indicated in the figure by a change of shading. Then follows a nearly dark interval, b, and after this the region c, showing greenish afterglow with continuous spectrum.

If a blue glass is used to cut out the  $\alpha$ -group of bands, then the intensity distribution of (blue-violet) light is approximately as represented by the curve d. The effect of the nitric oxide can be detected much further up stream than without the blue glass. The left-hand hump of the curve, of course, shows blue-violet light, due to the less refrangible  $\beta$ -bands, and the right-hand one blue-violet light of the continuous spectrum. No. 11, Plate 1, shows the spectrum of a tube of this kind, provided with a quartz window. The slit was a long one, and was placed as close up as possible, with its length parallel to the axis of the tube. The concentration of nitric oxide increases from below upwards. The extinction of the  $\beta$  and  $\gamma$  groups, and the replacement by the short continuous spectrum, is clearly seen.

In addition to the above cases, others have been investigated, but less thoroughly, and without quantitative observations on the rate of admission.

Nitrogen peroxide was prepared by liquefying the gas from heated lead nitrate. Vapour was taken off from the liquid straight into the apparatus, and, though it perhaps contained a trace of nitric oxide initially, this would pass off in the early stages of the distillation, leaving pure peroxide in the later stages. The later fractions gave, however, exactly the same results as the earlier ones.

These results were exactly similar in general character to those above recorded for nitric oxide, but the luminosities were much fainter. All the phenomena recorded in connection with fig. 2 were reproduced.

Nitrous Oxide.—The commercial compressed gas was used. It gave the  $\beta$  and  $\gamma$  groups, but no trace of the greenish glow with continuous spectrum obtained with large admissions of nitric oxide.

The  $\beta$  and  $\gamma$  bands were also obtained by admitting water vapour from a small water bulb with stopcock sealed on to the apparatus.

### § 5. Flame Spectra of Oxides of Nitrogen.

These were examined for comparison with the afterglow spectra. An ordinary small injector blowpipe, intended for oxygen and coal gas, was fed with nitric oxide and coal gas. The flame showed visually the greenish luminosity with continuous spectrum, which is observed when much nitric oxide is introduced into the afterglow. The colour of this light is very characteristic, and affords convincing evidence of its identity in the two cases.

The photographed spectrum of the blowpipe flame showed the  $\gamma$ -group of bands strongly, without any trace of the  $\beta$ -group.

The flame then produces two of the three spectra associated with nitric oxide in the afterglow, but not the remaining one.

One of the photographs is reproduced in Plate 1, No. 7. It shows, of course, the water vapour bands in addition to the bands introduced by nitric oxide.

Nitrous oxide with coal gas, in the same blowpipe, also gave the greenish continuous spectrum, and the  $\gamma$ -group without the  $\beta$ -group. But neither of the former was nearly so intense as with nitric oxide.

With air and coal gas neither of the spectra in question was observed.

With oxygen and coal gas something may be seen of the greenish colour round the tip of the flame, but it is known that oxidation of nitrogen occurs in the oxy-coal-gas flame, so that this observation throws no further light on the origin of the greenish continuous spectrum.

The fine photograph of the oxy-hydrogen flame spectrum made by Liveing and Dewar shows nothing of the  $\beta$  or  $\gamma$  groups.

The  $\beta$ -group of bands was not obtained from flames fed with oxides of nitrogen, even when the  $\gamma$ -group was very heavy from long exposure of the plate. Reis\* provisionally attributes two bands at  $\lambda$  268 and  $\lambda$  256, which he observed in the flame of cyanogen burning in oxygen, to the  $\beta$ -group. I find it difficult or impossible to accept this conclusion, for the bands in question are very inconspicuous members of the  $\beta$ -group, and it is contrary to all probability that they would be detected in preference to many much

stronger bands of this group. Moreover, Prof. Fowler has kindly examined a very excellent photograph of the flame of cyanogen burning in oxygen, which was taken in his laboratory, and finds no trace of these bands.

# § 6. Origin of \$\beta\$ and \$\gamma\$ Groups.

Since these groups are only obtained in the afterglow by adding oxygen-containing admixture, it would seem natural to attribute them to oxides of nitrogen formed.

Again, if we compare the least amount of oxygen required in various forms to produce the same (maximum) intensity, we find approximately

Nitric oxide	0.76
Oxygen	1.0
Carbon dioxide	40

Thus, oxygen as nitric oxide goes further than as free oxygen and much further than as earbon dioxide.

Again, the  $\gamma$ -group is developed in a blowpipe flame fed with nitric oxide but not in one fed with oxygen.

In spite of the apparent force of these arguments, I cannot definitely attribute the bands to nitric oxide, or any other oxide of nitrogen, for I have been unable to prove that the necessary oxidation occurs when oxygen is fed into active nitrogen.

To get some notion of how much oxidation is to be expected with the experimental arrangement used, suppose enough or more than enough oxygen to be fed into the active nitrogen stream to get the best spectroscopic effect. Then, to equal this effect, we should have to admit at least 21 c.c. of nitric oxide per hour instead of the oxygen. If the action of oxygen is in the actual formation of nitric oxide, we must look for some such quantity as 21 c.c. per hour to be formed.

The experiments made have proved clearly that the nitric oxide formed (if any) is less than 1 c.c. per hour.

The gas stream on its way to the pump was passed through a condenser tube, cooled in liquid air. This could be detached by loosening a ground joint and the contents tested with Griess' reagent.

Many tests were made with and without oxygen admitted to the afterglow. In either case there was generally some very slight reaction, indicating the presence of a trace of oxides of nitrogen. The amount of reaction was variable, but there was no indication that it was more when oxygen was admitted to the afterglow than when it was not. The origin of this slight reaction is presumably in some remaining traces of oxygen compounds present

along with nitrogen in the discharge tube, and giving rise to exidation. It must be remembered that at every test atmospheric pressure has to be admitted, in order to detach the cooled condenser, thus the uniform régime is necessarily disturbed.

Comparative experiments were made, introducing nitric oxide intentionally into the gas stream. The nitric oxide was diluted with nitrogen, to avoid dealing with an inconveniently small influx. No discharge was passed during these comparative tests, but the gas stream was as usual. A very strong reaction was obtained when the rate of admission was as much as 21 c.c. nitric oxide per hour. To reduce the reaction to what was obtained in the actual tests, the rate had to be reduced below 1 c.c. per hour.

These experiments prove, therefore, that oxidation of nitrogen does not occur when oxygen is admitted to the afterglow or, if it does, at all events not to a sufficient extent to allow us to attribute the  $\beta$  and  $\gamma$  emission to nitric oxide.

The same will apply to the higher oxides of nitrogen. These are formed at once by the action of active nitrogen on nitric oxide. Thus, in spite of the many new data obtained, it is not possible to make any distinct pronouncement as to what chemically is the vibrating system which gives rise to the  $\beta$  and  $\gamma$  groups. It can only be stated that both oxygen and nitrogen must be present. This unsatisfactory kind of result is by no means unexampled in spectroscopy. For instance, the "magnesium hydride" spectrum requires both magnesium and hydrogen for its production. Yet no chemical compound responsible for it has ever been proved to exist.

# § 7. Summary (a Selection only of the Facts Established).

- (1) The faint red bands 6394.45, 6468.53, 6544.81, and 6623.52, belonging to the first positive group, truly belong to the afterglow spectrum of nitrogen.
- (2) The second positive group is entirely absent from the afterglow spectrum.
- (3) The  $\beta$  and  $\gamma$  groups only appear when oxygen-containing gases are introduced into the afterglow, or are originally present in the nitrogen used.
- (4) Using nitrogen that only gives the  $\beta$  and  $\gamma$  bands very faintly, it is found that oxygen or nitric oxide added to the afterglow bring in the  $\beta$  and  $\gamma$  bands with a certain relative intensity, which may be called the standard. Carbon dioxide gives greater relative intensity to the  $\beta$ -bands, and carbon monoxide to the  $\gamma$ -bands.

<sup>\* &#</sup>x27;Roy. Soc. Proc.,' A, vol. 86, p. 58 (1911).

- (5) If nitric oxide or nitrogen peroxide is introduced in sufficient quantity into the afterglow, the  $\beta$  and  $\gamma$  groups disappear, and a visually greenish continuous spectrum, not extending into the ultra-violet, is substituted. Nothing like this is observed with the other oxygen-containing gases.
- (6) Nitric oxide in a blowpipe flame gives this same greenish continuous band, together with the  $\gamma$ , but not the  $\beta$ , group.
- (7) Chemical tests show that, when oxygen is introduced into the afterglow, there is no detectable oxidation of nitrogen, and certainly not nearly enough to account for the  $\beta$  and  $\gamma$  bands, on the view that these are due to nitric oxide generated. No definite conclusion is reached as to the origin of the  $\beta$  and  $\gamma$  groups, except that they require the presence of both nitrogen and oxygen.

#### DESCRIPTION OF PLATE.

- 1. Spectrum of nitrogen afterglow. The nitrogen purified with phosphorus, and elaborately dried. Shows chiefly mercury from the manometer, and cyanogen bands.  $\beta$  and  $\gamma$  bands faint.
- Effect of adding air to same afterglow, after the gas has been through discharge.
   β and γ groups very much enhanced.
- 3. Effect of adding carbon dioxide to afterglow of No. 1. Note that the  $\beta$ -bands are more intense relative to  $\gamma$ -bands than in No. 2.
- 4. Carbon monoxide added to afterglow of No. 1. Note that the β-bands are here much less intense relative to the γ-bands. The cyanogen bands, particularly that at 388, are strongly brought in.
- 5. A mixture of ethylene and oxygen brought into the afterglow. This also shows β and γ and cyanogen bands, like carbon monoxide, but the β-bands are not faint in this case. (Cf. No. 4.)
- 6. Small quantity of nitric oxide brought into afterglow.  $\beta$  and  $\gamma$  bands as with air.
- Nitric oxide in blowpipe flame. Note γ-group without β-group. Water vapour bands also conspicuous.
- 8. Large amount of nitric oxide introduced into afterglow, producing continuous band in less refrangible part of spectrum. Note contrast with No. 6.
- 9. Direct photograph through yellow screen of afterglow tube, with small amount of oxygen admitted in the middle of it.
- 10. Photograph of same, through blue screen, shows the great increase of violet and ultra-violet light due to development of  $\beta$  and  $\gamma$  groups, where the oxygen enters.
- 11. Spectrum photograph, showing the effect of increasing concentration of nitric oxide in the afterglow.

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- 11. Spectrum photograph, showing the effect of Increasing concentration of nitric oxide in the afterglow.

# The Selective Properties of the Copper Ferrocyanide Membrane.\* By Frank Tinker, D.Sc.

(Communicated by Sir Oliver Lodge, F.R.S. Received August 30, 1916.)

In a previous research dealing with the structure of semi-permeable membranes,† it has been shown that the copper ferrocyanide membrane is built up from colloidal particles having diameters ranging from 50 to 400  $\mu\mu$ ; also that the pores enclosed by these particles have an average diameter which, although large enough to allow passage to any non-colloidal molecule, is small enough to be entirely within the range of capillary effects. On the basis of these facts the hypothesis was advanced that the selective properties of colloidal membranes are due to selective adsorption; a copper ferrocyanide membrane immersed in cane-sugar solution, for instance, being permeable to the water and not to the cane sugar, because the water, rather than the sugar, is selectively adsorbed or "condensed" on to the membrane surface and into its capillaries.

The present research is an experimental investigation of this view. The measurements made herein consist in a determination of the change in concentration brought about by immersing more or less dry colloidal copper ferrocyanide in cane-sugar solutions of various strengths. The results obtained tend to confirm the adsorption hypothesis for this case at least.

# I. Experimental Method.

The method of experiment usually adopted was to shake up 10 grm. of colloidal copper ferrocyanide prepared as below with 100 c.c. of sugar solution for two days at room temperature (15° C.).‡ At the end of that time, the solution was cleared completely of the finely divided ferrocyanide with the aid of a powerful Delepine centrifuge developing a force of about 10,000 times gravity. Its optical rotation was then determined side by side with that of a blank sample of the original solution which had been treated similarly to it at all stages, except for the introduction of the ferrocyanide.

The colloidal copper ferrocyanide was prepared as follows:—A solution of 215 grm. of potassium ferrocyanide in  $1\frac{1}{2}$  litres of water was added to a solution of 250 grm. of copper sulphate, also dissolved in  $1\frac{1}{2}$  litres of water. The mixture was then diluted to 5 litres, churned up for a few hours, and

<sup>\*</sup> Being part of a Thesis approved for the Degree of Doctor of Science in the University of London.

<sup>†</sup> Tinker, 'Roy. Soc. Proc.,' A, vol. 92, p. 357 (1916).

<sup>‡</sup> Slight changes in temperature of one or two degrees centigrade have no measurable influence on the adsorption equilibrium.

the copper ferrocyanide suspended in it then centrifuged down. In order to free the colloid from most of the salts (mainly K<sub>2</sub>SO<sub>4</sub>) entangled in it,\* it was washed twice by churning with 5 litres of water for one day, the ferrocyanide being separated each time by the centrifuge as before. At this stage the colloidal ferrocyanide was in the form of a sticky clay. It was converted into a dry clay by wrapping it up in filter-paper pockets placed above absorbent lint in a series of centrifuge tubes (fig. 1), and then centrifuging

for a few hours. It was dried still further by steeping it in anhydrous ether for two days, the ether left attached to the ferrocyanide after decantation being removed by passing a current of dry air for one day over the colloid, kept at a temperature of from 30° C. to 45° C. So prepared, the ferrocyanide was obtained as a light brown, fluffy powder, which, although not absolutely dry, was found to take up moisture if left exposed to the atmosphere. Previous to use in the subsequent adsorption experiments, it was dried more thoroughly in the manner indicated in each case.†

Inasmuch as the changes in the concentration of the bulk of a solution due to adsorption are not very large, it was found necessary to introduce a high degree of refinement into the polarimetric measurements. Accordingly, many of the improvements introduced into polarimetric work by Dr. T. M.



Fra 1

Lowry‡ were adopted. The source of light, for instance, was a 600-c.p. Cowper-Hewitt silica mercury vapour lamp, as modified by Dr. Lowry. The beam from it was condensed without previous resolution into a Hilger polarimeter, and separated into its components after passing through the sugar solution by means of a small direct vision spectroscope placed in the polarimeter eyepiece. The readings for the mercury green line only were taken, the column of solution being 6 dm. in each case. The temperature at which the rotations were determined was 20° C., the Lowry thermo-regulator, bath, and water-jacketing system being employed.§ It was found that the

<sup>\*</sup> It is fatal to wash the colloid too thoroughly. If all the entangled salts are completely removed, the ferrocyanide subsequently forms with the sugar solution a sol which the centrifuge brings down only with extreme difficulty.

<sup>†</sup> The details of the preparation given above are all more or less essential for success. Unless care is exercised the ferrocyanide is apt to be obtained on drying in the form of a horny mass which is tough, highly compact, and unworkable.

<sup>†</sup> Lowry, 'Trans. Chem. Soc.,' vol. 103, p. 1063 (1913) 'Proc. Roy. Inst.,' April 18, 1913, and other papers.

<sup>§</sup> For a working knowledge of these things I am indebted to the valuable training Dr. Lowry gave me as a student with him. I am also much indebted to Sir Oliver Lodge for the provision of the instruments and materials in question.

solutions could be read quite easily to 0.01°, so that the experimental error on a difference of one or two degrees rotation was within one per cent.

In order to prevent slight changes in the concentration of the solutions due to fermentation, all vessels were invariably sterilised, and the solutions themselves rendered sterile before using by raising them to 90° C. for a few minutes.

Preliminary to the concentration experiments proper being carried out, the following experimental points were also ascertained:—

- (a) When the colloidal ferrocyanide is placed in the sugar solution, equilibrium is attained within a few hours. A series of 10-grm. samples of ferrocyanide placed in 100 c.c. of 20-per-cent. sugar solution (rotn. = 85·34° in a 6-dm. tube at 20° C.) gave rotations of 85·65°, 85·61°, 85·58°, 85·63°, after 5 hours, 1 day, 2 days, and 4 days respectively.
- (b) Different samples of ferrocyanide from the same stock alter the rotation of any sugar solution to almost but not quite the same extent. Thus, four 10-grm. samples from the same bulk increased the rotation of 100 c.c. of 20-per-cent. sugar solutions from 85·34° (in a 6-dm. tube) to 85·58°, 85·63°, 85·65°, 85·60° respectively. This difference is probably due to inavoidable inequalities in the colloidal condition of the ferrocyanide, even in similar samples. Very regular curves, connecting the change in concentration with the concentration itself, are therefore not to be expected.
- (c) Neither the colloidal ferrocyanide itself, nor the traces of potassium sulphate left in it, exert any hydrolysing effect on the sugar solutions under the conditions employed.

# II. Experimental Results.

In obtaining the following results, different bulk samples of ferrocyanide were used in the different series of experiments. It will be seen that these samples differed somewhat from one another in degree of dryness, according to the method of drying adopted. The object of varying this factor was to determine how the changes in colloidal condition induced thereby would affect the results.

The Tables are built up on the assumption that water only and no sugar is absorbed by the colloidal ferrocyanide.\* On this assumption, it is evident

\* This assumption is not quite correct. Sugar will be "adsorbed" to a certain extent also, at least into the outer layers of the surface film. In this case, if y is the weight of sugar absorbed from 100 c.c., and c is the concentration of the solution (grammes per 100 c.c.)  $x = \frac{100 \text{ (increase in rotation)}}{\text{rotation at equilibrium}} + \frac{100 y}{c}$ , x is thus really greater than the Tables would indicate.

that, if x grm. is the weight of water removed from 100 c.c. of the solution by shaking with the ferrocyanide,

Rotation at equilibrium = 
$$\frac{100}{100-x}$$
 (original rotation),

$$x = 100 \left( \frac{\text{increase in rotation}}{\text{rotation at equilibrium}} \right).$$

The last column in the Tables, headed "Total water absorbed by 100 grm. dry ferrocyanide," is calculated from the previous column by allowing for the amount of moisture originally in the colloid before immersion in the solutions. Thus, in Table II (bulk sample B), the true weight of the 10 grm. of ferrocyanide taken in each case is 9.311 grm., and in this case the column is given by the relation.

Total water absorbed at equilibrium

= 
$$100 \frac{\text{(Water removed from } 100 \text{ c.c.} + 0.689)}{9.311}$$

Table I.—Bulk Sample A of Copper Ferrocyanide. Dried for one day in steam oven. 10 grm. contained 0.00 grm. water (absolutely dry). October 7, 1915.

Weight of ferrocyanide shaken with 100 c.c.	Approximate strength of cane-sugar solution.	Original rotation of sugar solution.	Rotation at equilibrium.	Increase in rotation.	Water removed from 100 c.c.	Total water absorbed by 100 grm, dry ferrocyanide.
grm.	per cent.	0	٠	•	grnı.	grnı.
10	10	44 .85	45 17	0 .82	î ·82	18 ·2
10	20	83 .95	85 28	1 .28	1 .20	<b>15 ·</b> 0
10	40	151 -81	153 86	2 .02	1 .34	13 •4
10	60	205 .06	207 82	2.76	1 .32	18 ·2

<sup>\*</sup> The strength is given in grammes cane sugar added to 100 c.c. water. The rotations are those given by a 6 dm. tube.

Table II.—Bulk Sample B of Copper Ferroeyanide. Partially dried over conc. H<sub>2</sub>SO<sub>4</sub>. 10 grm. contained 0.689 grm. water. October 12, 1915.

Weight of ferrocyanida ahaken with 100 c.c.	Approximate strength of cane-sugar solution.	Original rotation of sugar solution.	Rotation of sugar solution at equilibrium.	Increase in rotation.	Water re- moved from 100 c.c. solution.	Total water absorbed by 100 grm, dry ferrocyanide.
grm. 10 10 10 10	per cent. 10 20 40 60	44 ·40 76 ·25 150 ·86 205 ·76	45 ·25 78 ·02 152 ·24 207 ·60	0 ·85 1 ·77 1 ·88 1 ·84	grm. 1·88 2·27? 1·24 0·89	grm. 23 *9  18 *0 14 *7

Table III.—Bulk Sample C of Copper Ferrocyanide. Partially dried by current of air at 80° C. for three hours. 10 grm. contained 1.382 grm. water. November 29, 1915.

Weight of ferrocyanide shaken with 100 c.c.	Approximate strength of cane-sugar solution.	Original rotation of sugar solution.	Rotation of sugar solution at equilibrium.	Increase in rotation.	Water re- moved from 100 c.c. solution.	Total water absorbed by 100 grm. dry ferrocyanide.
grm.	per cent.	۰	. 0	Ö	grm.	grin.
20	<b>.</b> 5	25 .58	26 .04	0.51	1 955	<b>27</b> ·0
20	10	45 19	46 78	0.54	1 153	22 .7
10	20	88 ·11	88 .61	0 .20	0.563	22 .5
10	40	153 .28	154 -11	0.88	0.588	22 ·2
10	60	210 .50	211 .37	0.87	0.424	20 .8

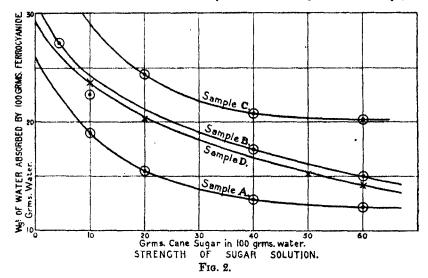
Table IV.—Bulk Sample D of Copper Ferrocyanide. This sample was not dried at all. 10 grm. contained 3.14 grm. water. It will be noted that the sugar solutions were weakened in this case. In spite of this, however, the total water absorbed by 100 grm. of dry ferrocyanide is of the same order as in the other three cases. September 7, 1915.

Weight of ferrocyanide shaken with 100 c.c.	Approximate strength of cane-sugar solution.	Original rotation of sugar solution.	Rotation of sugar solution at equilibrium.	Increase in rotation.	Water re- moved from 100 c.c. solution,	Total water absorbed by 100 grm. dry ferrocyanide.
grm.	per cent.	0	0	0	grm.	grm.
5	<b>1</b> 0	443.2	44.00	-0.82	-0.728	24·5
5	20	83 21	82 48	-0.73	-0.885	20 1
5	30	118 -55	117 .55	-1.00	-0.855	21 0
5	. 40	149 .47	148 15	-1:32	-0.881	20.0
5	50	179 03	177 14	-1 :89	-1.065	14 .9
5	60	204 70	202 50	-2 .50	-1 090	14 0

Fig. 2 shows graphically the relation between the concentration of the solution and the total water absorbed by 100 grm. of dry ferrocyanide for each of the four samples chosen. It will be seen that water is absorbed by the ferrocyanide from all the sugar solutions to quite a considerable extent. The amount absorbed decreases as the strength of the solution increases, and varies from about 30 grm. of water from pure water to 13 or 14 grm. of water from a 60-per-cent. solution of cane sugar. The curves show no tendency, however, to approach the x axis, but rather to become horizontal

<sup>\*</sup> Sample C gives a somewhat higher curve than the other three samples. Further experiments with fresh samples showed that this behaviour is characteristic of samples dried slowly in air at high temperatures (80-100° C.). The samples dried like this turn almost black, apparently because some of the ferrocyanide is decomposed into copper oxide. The results for this sample are therefore not so reliable as for the other three samples.

when the moisture-content is about 14 grm. in the case of strong solutions. This fact would indicate that the ferrocyanide forms a hydrate Cu<sub>2</sub>FeCy<sub>6</sub>,3H<sub>2</sub>O,



which corresponds to a moisture-content of 15.7 grm, water per 100 grm, dry ferrocyanide. The probability that copper ferrocyanide forms a stable hydrate in all except the very strongest aqueous solutions was noted by Graham on grounds quite different from the present one.\*

Postulating the existence of this stable hydrate in solutions of all strengths, we have now to explain in what manner the moisture in excess of the amount which corresponds to this hydrate is taken up, whether by extra hydration of the copper ferrocyanide molecules, or by solution in the colloidal phase, or by "adsorption" proper on to the surfaces of the colloidal particles. It will be seen that the facts are in agreement with the adsorption hypothesis; for there is no simple relation between the amount taken up and the concentration; neither is the amount taken up by a given weight of dry ferrocyanide from a solution of given strength a constant, as it should be if the water were either dissolved water or hydrate water. This latter variation in amount of water taken up can only be due to variation in the surface area of the colloid in the different samples, causing a corresponding increase or decrease in the adsorbing capacity.

# III. Application of the Results to the Theory of Osmosis.

The above experiments bring out several facts with regard to the copper 'ferrocyanide membrane.

\* Graham, "Liquid Diffusion applied to Analysis," 'Collected Papers,' p. 583.

- (1) The membrane is really composed of colloidal particles of copper ferrocyanide hydrate, probably Cu<sub>2</sub>FeCy<sub>6</sub>,3H<sub>2</sub>O.
- (2) The colloidal particles of copper ferrocyanide hydrate in the membrane adsorb water selectively from solutions of cane sugar, without taking up the sugar to any appreciable extent at the same time.
- (3) The amount of water adsorbed depends on the strength of the sugar solution in which the membrane is placed, decreasing as the solution gets stronger.

The selective adsorption hypothesis previously advanced as the reason for selective permeability follows immediately from the second of these facts. It is self-evident that if the sugar cannot get into the membrane because of the selective surface effects, neither can it get through the membrane for the samo reason.

Likewise from the third fact we can arrive at the cause for osmotic flow. If pure water, for instance, is on one side of a copper ferrocyanide membrane and cane-sugar solution is on the other, the adsorbed moisture-content of the membrane and, therefore, the adsorbed moisture pressure also, will be greater on the water side of the membrane than it is on the solution side. A continual flow across the membrane from the water to the solution will therefore take place, equilibrium being impossible so long as there is a concentration difference between the liquids bathing the two sides.\*

It may be mentioned in passing that, in principle, this view of the cause of osmotic flow was first advanced by Graham, who showed that gelatinous membranes swell more in contact with pure water than they do in contact with certain salt solutions. Graham accordingly explained osmotic flow by the hypothesis that the water side of the membrane is more highly "hydrated" than the solution side.† In this connection it is also interesting to note that similar results to the above have also been obtained by Prof. Adrian Brown with the seeds of common barley.‡ These seeds form an ideal osmotic system, in that they are really a mass of colloidal material (starch), surrounded by a semi-permeable membrane. Prof. Brown has shown that, when the seeds are immersed in aqueous solution of cane sugar, common salt, and other solutes impermeable to the membrane, the amount of water absorbed by the colloidal contents is less than that absorbed by the seeds from pure water, being diminished to about one-half

<sup>\*</sup> I.e., in the absence also of a pressure being applied to the solution in order to prevent diffusion.

<sup>† &#</sup>x27;Phil. Trans.,' 1861, pp. 183-224 ("Liquid Diffusion applied to Analysis," Section 8). This view has also been revived by Trouton (Presidential Address, British Association, Section A, 1914).

<sup>† &#</sup>x27;Roy. Soc. Proc.,' B, vol. 81, p. 82 (1909).

the latter amount in the case of molar solutions. Prof. Brown and the present author have, however, lately shown\* that the amount of solvent taken up by the seeds depends also on the amount of solute taken up simultaneously, being at a minimum when the membrane is truly semi-permeable to the solute, equal to the amount taken up from pure water when the membrane exerts no selective action, and actually greater than the amount taken up from pure water when the seeds adsorb the solute selectively.

In the light of the above facts, it is evident that we can no longer regard the actual colloidal membrane as a geometrical plane perforated with small holes. It is rather a separate phase in the osmotic system, into which the solvent can diffuse from both the pure solvent and solution. The solvent flows from the pure solvent to the solution, because the former generates a greater solvent pressure and concentration inside the membrane than does the latter, just as it also generates a greater concentration and pressure inside the vapour phase. The phenomenon of osmotic flow thus becomes similar in nature to that of vapour flow, and both have their origin in the greater "activity" of the pure solvent. But, although we are justified in concluding that the two phenomena are similar, we must not assume that they are identical. In particular, we must guard against postulating that the solvent travels across a semi-permeable membrane as vapour,+ for the experimental work which has been described shows that the concentration of the solvent inside the membrane is much greater than it is inside the vapour phase proper, owing to the fact that the colloidal particles of the membrane condense it on to their surfaces. The solvent travels across the membrane in the adsorbed condition, and as such is neither liquid nor vapour.

#### IV. Summary.

The selective properties of copper ferrocyanide have been studied by measuring the change in solution concentration which takes place when the dry colloid is immersed in cane-sugar solutions of various strengths. It is found that the solutions become stronger, owing to the fact that the water and not the sugar is taken up selectively by the ferrocyanide. The experimental results are in accordance with the hypothesis that a colloidal hydrate Cu<sub>2</sub>FeCy<sub>6</sub>,3H<sub>2</sub>O is first formed, and that this colloidal hydrate takes up still more moisture by adsorption. The amount of "adsorbed" moisture taken up by the colloid decreases as the strength of the solution increases.

The fact that colloidal ferrocyanide adsorbs water selectively from cane-

<sup>\* &#</sup>x27;Roy. Soc. Proc.,' B, vol. 89, p. 373 (1916); ibid., B, vol. 89, p. 119 (1915).

<sup>†</sup> Cf. Callendar's vapour pressure theory.

sugar solutions without taking up the sugar at the same time supports the author's theory that the property of selective permeability is (in the case of colloidal membranes) a result of preferential adsorption.

It is also shown in the above paper that the side of a membrane in contact with pure water has a greater moisture content than the side in contact with sugar solution. This fact supports the hypothesis—first advanced by Graham on experimental grounds—that osmosis across the membrane takes place because pure water induces a greater moisture pressure and concentration inside the membrane than the solution does.

On the Ordinary Convergence of Restricted Fourier Series.

By Prof. W. H. Young, Sc.D., F.R.S.

(Received October 11, 1916.)

§ 1. The necessary and sufficient condition that a trigonometrical series\* should be a Fourier series is that the integrated series should converge to an integral throughout the closed interval of periodicity, and should be the Fourier series, accordingly, of an integral. Conversely, starting with the Fourier series of an integral and differentiating it term by term, we obtain the Fourier series of the most general type, namely, one associated with any function possessing an absolutely convergent integral.

If the Fourier series which is differentiated is not the Fourier series of an integral, but of a function which fails to be an integral, at even a single point, the derived series will not be a Fourier series.

The series so obtained, namely, by differentiating term-by-term the Fourier series of a function which, without being an integral in the whole closed interval of periodicity, is an integral in one or more sub-intervals, I have found it convenient in a recent paper† to call "restricted Fourier series." I retain the term "Fourier," because such series possess, in the interval or

<sup>\*</sup> It is convenient to suppose the trigonometrical series to have no constant term, or toregard the integrated series as a series obtained from the original series by interchanging the coefficients of  $\sin nx$  and  $\cos nx$ , changing the sign of one of them, and dividing both by n. The integral to which the integrated series converges is accordingly a periodicfunction. By integral we mean, as usual, absolutely convergent or Lebesgue integral.

<sup>+ &</sup>quot;On the Convergence of the Derived Series of Fourier Series," read at the June-Meeting, 1916, of the L.M.S. and recently presented to that Society.

intervals to which they are "restricted," several of the properties of Fourier series, so that they can be employed in analysis in some of the ways in which ordinary Fourier series have been used.

There is, however, one important difference between the new and the old types of Fourier series. In dealing with the former, we can in general only employ the method of summation due to Cesàro, index unity at least. The theorems which continue to hold for restricted Fourier series in the interval to which they are restricted are obtained by modifying suitably theorems relating to Fourier series in which Cesàro convergence occurs. For more information on this point I must refer my readers to the paper just cited. It will suffice for our present purposes to refer to only one of these properties. It is known that the behaviour of a Fourier series as regards convergence, or mode of oscillation, at a particular point x of the interval  $(-\pi, \pi)$  of periodicity, depends only on the nature of the associated function in the neighbourhood of the point, this neighbourhood being taken as small as we please, and the method of summing the series, or of obtaining its upper and lower functions, peak and chasm functions, etc., being the ordinary classical one.

It is remarkable both that this theorem fails in the case of restricted Fourier series, and that it becomes true when the summation is performed in the Cesaro manner, index  $\geq 1$ .

Thus tests for the ordinary convergence of a restricted Fourier series of a type analogous to the known ones for Fourier series cannot exist, but only tests for the Cesàro convergence analogous to those for the Cesàro convergence of ordinary Fourier series.

And again only those theorems relating to the integration term-by-term of a Fourier series, after multiplication by another function, in which the convergence employed is of the Cesàro type, have their analogues in the general theory of restricted Fourier series.

To secure the ordinary convergence of a restricted Fourier series at a point or in an interval, and the holding good of integration theorems which involve ordinary convergence in an interval, conditions must be fulfilled which concern not only the neighbourhood of the point, or the interval considered, but also the whole of the rest of the interval of periodicity. In other words, additional hypotheses of a novel type will have to be made. In the present communication to the Society I propose to initiate the new theory which thus arises, by considering a case which, though special in character, is probably the most important of all the cases that can present themselves. I assume that the failure of the derived series to be a Fourier series is due to the fact that, at a finite number of points, the function associated with the series from which it is derived fails to be an integral. In other words this function is an integral

over every sub-interval which does not contain any of the points in question, and over such intervals only.

The main general auxiliary theorem obtained is that if  $\mathbf{F}(t)$  is the function associated with the original Fourier series, and has accordingly f(t), the function associated with the restricted Fourier series, for its differential coefficient almost everywhere, then the restricted Fourier series behaves in every interval not containing one of the points  $k_1, k_2, \ldots, k_s$  at which  $\mathbf{F}(t)$  ceases to be an integral, exactly like a Fourier series, provided:

- (1)  $(x-k_r)$   $\mathbf{F}(x)$  is an integral in some interval containing  $k_r$ , for r=1, 2, ..., s; and converges to zero, as  $x \to k_r$ ;
- (2) if  $q_r(x)$  denote any function which, except in a certain sub-interval of the interval  $(-\pi, \pi)$ , surrounding  $x = k_r$ , is a periodic integral, and in that exceptional sub-interval is equal to F(x), then the coefficients of the derived series of the Fourier series of  $q_r(x)$  converge to zero, for r = 1, 2, ..., s.

It will be noticed that, in the case of a single exceptional point  $k_r$ , the second of the pair of conditions, thus shown to be sufficient, is certainly a necessary condition for a trigonometrical series to converge; its terms must, like those of any other series, themselves converge to zero. Moreover, as is well known, if this convergence holds throughout an interval, however small, the coefficients must themselves converge to zero.

With regard to the first condition, I show in the present paper that all known conditions imposed upon f(x), to secure the fulfilment of (2), involve at the same time the truth of (1). The conditions in question are those which I have recently communicated to the Society\*; they lead at once, among others, to the following theorems:—

If as 
$$u \to 0$$
, we have for  $r = 1, 2, ..., s$ ,

(i) 
$$\mathbf{F}(k_r+u)-\mathbf{F}(k_r-u)\to 0,$$

(ii) 
$$F(u+k_r) - F(u-k_r) - \frac{1}{u} \int_0^u F(t+k_r) dt + \frac{1}{u} \int_0^u F(t-k_r) dt = 0,$$

and if further

(iii) 
$$\mathbf{F}(u+k_r) - \frac{1}{u} \int_0^u \mathbf{F}(t+k_r) dt$$

is an integral for some interval containing u = 0, F(x) being the function associated with the Fourier series, from which the restricted Fourier series was derived, then the behaviour of the latter series at any point other than one of

\* "On the Order of Magnitude of the Coefficients of a Fourier Series," 'Roy. Soc. Proc.,' A, vol. 93, p. 42. For simplicity, the conditions are stated separately for an odd and an even function, and the singular point is supposed to be at the origin. The transition to the case contemplated in the present paper is of course immediate.

the exceptional points  $k_1, k_2, ..., k_s$ , depends only on the nature of F(x) in the neighbourhood of the point considered, and, therefore, only on the function f(x) = F'(x) associated with the restricted Fourier series.

Again, if, as  $u \to 0$ , we have for r = 1, 2, ..., s,

(i) 
$$F(u+k_r)-F(k_r-u)\to 0,$$

(ii) Lt 
$$u[f(k_r+u)] = \text{Lt } u[f(k_r-u)],$$

both these limits accordingly existing,

(iii) 
$$\frac{1}{u} \int_0^u \left| \frac{d}{dt} \left\{ t^2 f(t+k_r) \right\} \right| dt$$

is a bounded function of u, or, more generally,

(iiia) 
$$\frac{1}{u} \begin{bmatrix} u \\ 0 \end{bmatrix} d \left\{ t^2 f(t+k_r) \right\}$$

is a bounded function of u; the notation being as in the preceding theorem, then the same conclusion follows.

§ 2. These theorems take a very simple form if we specialise the character of the function further. Thus, we may, for example, replace the conditions (i), (ii), and (iii) of the former of these two theorems by the single condition that uf(u) is an even function of bounded variation which has the unique limit zero, as  $u \to 0$ , and thus obtain immediately, among others, the theorem:—

If uf (u) is an even function of bounded variation in the whole interval  $(-\pi, \pi)$  of periodicity, and has the unique limit zero, as  $u \to 0$ , then the restricted Fourier series associated with f(x) converges ordinarily at all points of the interval.

We may also replace the corresponding conditions in the second theorem by the condition that  $w^2f'(u)$  is an even function, which approaches zero, as  $u \to 0$ , while f(u) is itself a function of bounded variation in every interval not containing the origin, and so obtain the theorem that the restricted Fourier series associated with such a function f(x) converges everywhere, except at the origin.

Moreover, at the different points  $k_1, k_2, ..., k_s$ , of the fundamental theorem, we may, of course, secure the fulfilment of the corresponding condition by hypotheses, varying with the value of the subscript.

Closely connected with the subject of the paper are certain theorems depending on the uniform convergence to zero of that portion of the integral representing the *n*th partial summation, the treatment of which forms the main difficulty in these investigations. This uniformity is secured, like the convergence itself, by the hypotheses made. These additional theorems are those alluded to at the beginning of this introduction; their statement and proof will be found below.

§ 3. We begin by explaining some of the circumstances under which we may differentiate an integral of the form

$$\int_a^b f(x\pm u)g(u)\,du$$

under the sign of integration. In the succeeding theorems we encounter two such cases:—

(i) When f(t) has a differential coefficient at every point of the interval (a, b), and this differential coefficient is a bounded function of t, while g(t) is summable.

We may then multiply the bounded sequence

$$\{f(x+h\pm u)-f(x\pm u)\}/h$$

by g(u) and integrate term by term, which gives us the required result,

$$\frac{d}{dx}\int_{a}^{b} f(x\pm u) g(u) du = \int_{a}^{b} f'(x\pm u) g(u) du;$$

(ii) when f(t) and g(t) are both integrals for all the values of their arguments involved in the integral.

In this case writing

$$\mathbf{F}(t) = \int_0^t f(t) \, dt,$$

we have, integrating by parts,

$$\int_a^b f(x+u) g(u) du = \left[ F(x+u) g(u) \right]_a^b - \int_a^b F(x+u) g'(u) du,$$

which may be differentiated by case (i), giving,

$$\frac{d}{dx} \int_a^b f(x+u) g(u) du = \left[ g(u) f(x+u) \right]_a^b - \int_a^b g'(u) f(x+u) du$$
$$= \int_a^b g(u) f'(x+u) du,$$

which is the required result. The same reasoning gives the required result when we have f(x-u) instead of f(x+u).

We have here supposed the limits of integration independent of x; in the contrary case we must, of course, add on corresponding terms to the result of integration under the integral sign.

§ 4. It will also be convenient to prefix the following two Lemmas:— LEMMA 1.—If in a closed interval  $(-\epsilon, \epsilon)$ , G (x) is an integral which vanishes when x = 0, then the limits, as  $n \to \infty$ , of

$$p\int_{-\epsilon}^{\epsilon}G\left(x\right)_{\sin}^{\cos}px\,dx,\qquad (p=n+\frac{1}{2}),$$

can be made as small as we please by making e conveniently small.

In fact, integrating by parts, the integral which appears vanishes by the Theorem of Riemann-Lebesgue, and the expression in square brackets is as small as we please.

LEMMA 2.—If tf (t) is an integral in the closed interval of periodicity and the coefficients of the derived series of the Fourier series of f (t) converge to zero, then

Lt 
$$\left\{ \int_{-\pi}^{\pi} pf(t) \cos pt \, dt - \sin p\pi \left[ f(\pi) + f(-\pi) \right] \right\}$$
  
= 0,  $(p = n + \frac{1}{2})$ . (I)

For, denoting the integral whose limit is considered by I,

$$I = \int_{-\pi}^{\pi} pf(t) \cos nt \, dt - \int_{-\pi}^{\pi} pf(t) (1 - \cos \frac{1}{2}t) \cos nt \, dt - \int_{-\pi}^{\pi} pf(t) \sin \frac{1}{2}t \sin nt \, dt.$$

The first integral approaches zero, being 1+1/2n times one of the coefficients of the derived series.

The second and third integrals are of the form

$$p\int_{-\pi}^{\pi}g(t)\frac{\cos}{\sin} nt dt,$$

where g(t) is an integral, since, by hypothesis tf(t) is an integral.

Integrating by parts, this becomes

$$(1+1/2n)\left[\left(g(t)\frac{\sin nt}{-\cos nt}\right)^{\pi}_{-\pi}-\int_{-\pi}^{\pi}g(t)\frac{\sin nt}{-\cos nt}dt\right]$$

in which the integral approaches zero by the Theorem of Riemann-Lebesgue.

The bracket expression is zero when it involves the sine, and when it involves the cosine is

$$-[g(\pi)+g(-\pi)]\cos n\pi = -[f(\pi)+f(-\pi)]\cos n\pi,$$

whence, since  $\cos n\pi = \sin p\pi$ , and this term appears in (I) with minus sign, the required result follows.

Similarly

$$\operatorname{Lt}_{n\to\infty} \int_{-\pi}^{\pi} pf(t) \sin pt \, dt = 0, \qquad (p = n + \frac{1}{2}). \tag{II}$$

§ 4. The following auxiliary theorem is an immediate consequence of the known theory of Fourier series:—

THEOREM I.—If (i) the associated function F(u) of a Fourier series is an integral in the closed interval (x-c, x+e) of its interval of periodicity  $(-\pi, \pi)$ , so that it has accordingly an absolutely integrable differential coefficient, f(u), day, existing almost everywhere in the closed interval (x-e, x+e); and if

(ii) 
$$Q = \frac{d}{dx} \int_{a}^{\pi} [F(x+u) + F(x-u)] \sin(n+\frac{1}{2}) u \operatorname{cosec} \frac{1}{2} u \, du \to 0, \quad (n \to \infty),$$

then the upper and lower functions of the derived series of the Fourier series of F(u) at the point x depend only on the properties of f(u) in a neighbourhood of the point x, as small as we please, and will be the same as those of the Fourier series of any absolutely integrable function, which agrees with f(u) in the closed interval (x-e, x+c).

Denote by  $s_n$  the *n*th partial summation of the derived series in question, then, by the usual theory,

$$s_{n} = \frac{1}{2\pi} \frac{d}{dx} \int_{0}^{\pi} \left[ (\mathbf{F} x + u) + \mathbf{F} (x - u) \right] \sin \left( n + \frac{1}{2} \right) u \operatorname{cosec} \frac{1}{2} u \ du.$$

and therefore, by condition (ii), the upper and lower limits of  $s_n$  are the same as those of

$$\frac{1}{2\pi} \frac{d}{dx} \int_0^a \left[ \mathbf{F}(x+u) + \mathbf{F}(x-u) \right] \sin(n+\frac{1}{2}) u \operatorname{cosec} \frac{1}{2} u \, du.$$

They are, therefore, by § 2, the same as the limits of

$$\frac{1}{2\pi} \int_0^e [f(x+u) + f(x-u)] \sin(n + \frac{1}{2}) u \operatorname{cosec} \frac{1}{2} u \, du. \tag{1}$$

This proves the theorem. In fact, if  $f_1(u)$  be any absolutely integrable function, agreeing with f(u) in (x-e, x+e), then, by the known theory,

$$\int_{-\pi}^{\pi} [f_1(x+u) + f_1(x-u)] \sin(n+\frac{1}{2}) u \csc(\frac{1}{2}u du \to 0), \qquad (n\to\infty);$$

and therefore the limits of the partial summations of the Fourier series of  $f_1(u)$  at the point x are the same as those of the expression (1).

COR. 1.—If in condition (ii) the convergence to zero at a point or in an interval is uniform, the restricted Fourier series of f(x) and the Fourier series of  $f_1(x)$  will have the same peculiarities with regard to uniformity, or non-uniformity, of convergence, or oscillation, at the point, or in the interval.

COR. 2.—Under the same circumstances as in Cor. 1, we may, in integration theorems involving integration term-by-term of a Fourier series when multiplied by a function g(x) which is absolutely integrable, substitute for the Fourier series the restricted Fourier series of a function f(x) which agrees with the associated function  $f_1(x)$  of the Fourier series in a sub-interval, provided the range of integration be restricted to that sub-interval.

In fact the difference between the nth partial summation of the restricted Fourier series and that of the Fourier series converges uniformly to zero, and therefore continues to do so when multiplied by any absolutely integrable function g(x), and integrated term-by-term.

§ 5. We have now to transform condition (ii) of the theorem just given in a manner suitable for the purposes in hand.

THEOREM II.—(i) If, outside the interval (x-e, x+e), F(u) is everywhere an integral, except at the finite number of points  $k_1, k_2, \ldots, k_s$ ; and if

(ii) for each r = 1, 2, ..., s, the expression

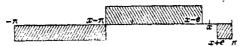
$$R = \int_{-\pi}^{\pi} F_{\tau}(u) \cos p (x_{\tau} - u) \frac{1}{2} p \operatorname{cosec} \frac{1}{2} (x_{\tau} - u) du$$

$$+\mathbf{F}_r(\epsilon)\sin p(x_r-\epsilon)\operatorname{cosec}\frac{1}{2}(x_r-\epsilon)-\mathbf{F}_r(-\epsilon)\sin p(x_r+\epsilon)\operatorname{cosec}\frac{1}{2}(x_r+\epsilon),$$

where  $\mathbf{F}_r(u)$  denotes  $\mathbf{F}(u+k_r)$ , and  $x_r = x-k_r$  and where p has, for brevity, been written for  $n+\frac{1}{2}$ , has, as  $n \to \infty$ , limits which are as small as we please, e being conveniently small, then the expression

$$Q = \frac{d}{dx} \int_{a}^{\pi} \left[ F(x+u) + F(x-u) \right] \sin\left(n + \frac{1}{2}\right) u \operatorname{cosec} \frac{1}{2} u \, du \to 0, \quad (n \to \infty).$$

For simplicity we may suppose that the extremities of the interval of periodicity are not included among the points  $k_r$ . No loss of generality is hereby occasioned.



For definiteness, suppose x positive.

The points  $k_r$  fall into two classes, those which lie in  $(x-\pi, x-e)$ , and those which lie in  $(x+e, \pi)$  or in  $(-\pi, x-\pi)$  (see figure).

As u increases from e to  $\pi$ , x-u will pass over points of the former class only, and (x+u) over points of the latter class only.

First let  $k_r$  denote one of the first class, and consider the expression

$$Q_1 = \frac{d}{dx} \int_{\epsilon}^{\pi} \mathbf{F}(x-u) \sin\left(n + \frac{1}{2}\right) u \operatorname{cosec} \frac{1}{2} u \, du.$$

Then, supposing there are s' such points, we divide up the interval  $(e, \pi)$  into 2s'+1 intervals. These intervals consist of (i) the two end-intervals  $(e, x-k_1'-\epsilon)$  and  $(x-k_{\epsilon'}+\epsilon, \pi)$ , and other corresponding intervals which do not contain the points  $x-k_r'$ , (ii) intervals of the type  $(x-k_r'-\epsilon, x-k_r'+\epsilon)$ . Consider the portion of  $Q_1$  due to an interval of the first class. This is of the type

$$\frac{d}{dx} \int_{x-u+s}^{x-\beta-\epsilon} \mathbf{F}(x-u) \sin\left(u+\frac{1}{2}\right) u \csc \frac{1}{2} u \, du$$

the integrand having no singularities with respect to x-u or u, so that, by § 2, this portion of  $Q_1$  may be differentiated in the usual way, giving us three terms, one of which is the integral obtained by omitting d/dx in

the preceding expression and writing f for F, and accordingly has the unique limit zero, and the other two are:

$$F(\beta + \epsilon) \sin p (x - \beta - \epsilon) \operatorname{cosec} \frac{1}{2} (x - \beta - \epsilon) - F(\alpha - \epsilon) \sin p (x - \alpha + \epsilon) \operatorname{cosec} \frac{1}{2} (x - \alpha + \epsilon).$$

In the case of the two end-intervals which belong to this class, one only of these two latter terms, of course, appears.

Next consider the portion of  $Q_1$  due to an interval of the second class. This is of the type

$$\frac{d}{dx} \int_{x-a-\epsilon}^{x-a+\epsilon} \mathbf{F}(x-u) \sin pu \operatorname{cosec} \frac{1}{2} u \, du,$$

which may be written

$$\frac{d}{dx} \int_{-t}^{t} \mathbf{F}(t+\alpha) \sin p(x-\alpha-t) \csc \frac{1}{2} (x-\alpha-t) dt,$$

where, by § 2, the differentiation may be performed under the integral sign. We thus get two terms, one of which has the unique limit zero, by the Theorem of Riemann-Lebesgue, while the other is

$$p\int_{-\epsilon}^{\epsilon} \mathbf{F}(t+\alpha)\cos p(x-\alpha-t)\csc \frac{1}{2}(x-\alpha-t)dt.$$

Collecting our results so far, and bearing in mind that, in the statement of condition (ii),  $x_r$  stands for  $(x-k_r)$ , and  $F_r$  (u) for  $F(u+k_r)$ , we see that, as far as  $Q_1$  is concerned, the singular points of the first of the two classes, into which we had divided them, give us terms precisely of the type stated in the enunciation of the theorem.

Next consider

$$Q_2 = \frac{d}{dx} \int_{\cdot}^{\pi} \mathbf{F}(x+u) \sin pu \operatorname{cosec} \frac{1}{2} u \, du.$$

We shall have work of precisely the same kind to perform as before in dealing with the first class of intervals. In the second class we shall write,

$$u = k_r^{\prime\prime} - x + t,$$

and paying attention to the sign of  $\epsilon$ , we shall find that, for  $Q_2$  also, the condition (ii) contains expressions to which we are actually led by our process. Thus our theorem is proved.

§ 6. It should be noticed that in the preceding theorem we have only used the condition that the singularities of F(u) are point singularities, in demanding merely that the expressions R can be made as small as we please, by taking conveniently small. If we require R to converge to zero, the singularities may be any we please inside the corresponding intervals.

In the next auxiliary theorem, about to be given, it is, however, essential that the points at which F(x) is not an integral should be finite in number.

**THEOREM III.**—(i) If outside the interval (x-e, x+e), F(u) is everywhere an integral, except at the finite number of points  $k_1, k_2, \ldots, k_s$ ;

- (ii)  $tF(t+k_r)$  is for each value of r=1, 2, ..., s, and an appropriate sufficiently small range of values of t, including t=0, an integral which converges to zero, as  $t\to 0$ ;
  - (iii) The expressions

$$p\int_{-\epsilon}^{\epsilon} \mathbf{F}(t+k_{\tau}) \frac{\cos}{\sin} pt \, dt \mp \mathbf{F}(\epsilon+k_{\tau}) \frac{\sin}{\cos} p\epsilon - \mathbf{F}(-\epsilon+k_{\tau}) \frac{\sin}{\cos} p\epsilon$$

have, as  $n \to \infty$ , limits all of which may be made as small as we please, by making  $\epsilon$  conveniently small; then the expressions which occur in Theorem II (ii), viz.,

$$R = \int_{-\epsilon}^{\epsilon} F_r(u) \cos p(x_r - u) \frac{1}{2} p \operatorname{cosec} \frac{1}{2} (x_r - u)$$

$$+ F(\epsilon) \sin p(x_r - \epsilon) \csc \frac{1}{2}(x_r - \epsilon) - F(-\epsilon) \sin p(x_r + \epsilon) \csc \frac{1}{2}(x_r + \epsilon)$$
 have limits which are as small as we please,  $\epsilon$  being conveniently small.

We have to consider the limiting value, or values, of expressions of the type

$$p\int_{-\epsilon}^{\epsilon} \mathbf{F}_{r}(u)\cos p(x_{r}-u)\operatorname{cosec}\frac{1}{2}(x_{r}-u)du + \mathbf{F}_{r}(\epsilon)\sin p(x_{r}-\epsilon)\operatorname{cosec}\frac{1}{2}(x_{r}-\epsilon)$$

$$-F_r(-\epsilon)\sin p(x_r+\epsilon)\operatorname{cosec}\frac{1}{2}(x_r+\epsilon)=A+B+C$$
, say.

Write

then

$$\operatorname{cosec} \frac{1}{2} (x_r - u) = \operatorname{cosec} \frac{1}{2} x_r + u g(x_r, u),$$

 $B+C = \{F_r(\epsilon)\sin p(x-\epsilon) - F_r(-\epsilon)\sin p(x_r+\epsilon)\} \operatorname{cosec} \frac{1}{2}x_r + \{\epsilon F(\epsilon)g(x_r,\epsilon)\sin p(x_r-\epsilon) + \epsilon F_r(-\epsilon)g(x_r,-\epsilon)\sin p(x_r+\epsilon)\},$ 

where the quantity inside the second curly bracket is as small as we please, when  $\epsilon$  is chosen conveniently small, since, by hypothesis (ii),  $u\mathbf{F}_r(u)$  approaches zero, when  $u \to 0$ , and  $g(x, \pm \epsilon) \sin p(x \mp \epsilon)$  is bounded.

Thus we may replace B+C by

$$\sin px \cos pe_r \csc \frac{1}{2}x_r [F_r(e) - F_r(-e)]$$

$$-\cos px_r\sin p\epsilon \operatorname{cosec} \frac{1}{2}x_r \left[ F_r(\epsilon) + F_r(-\epsilon) \right]. \quad (1)$$

Let us write

$$\mathbf{A} = \mathbf{L}\cos px_r + \mathbf{M}\sin px_r,$$

where

$$\mathbf{L} = p \int_{-\epsilon}^{\epsilon} \mathbf{F}_{r}(t) \cos pt \operatorname{cosec} \frac{1}{2} (x_{r} - t) dt = \operatorname{cosec} \frac{1}{2} x_{r} \int_{-\epsilon}^{\epsilon} p \, \mathbf{F}_{r}(t) \cos pt dt + \int_{-\epsilon}^{\epsilon} pt \, \mathbf{F}_{r}(t) g(x_{r}, t) \cos pt dt.$$

The integral last written down being as small as we please, by Lemma 1, since  $tF_r(t)$  and  $g(x_r, t)$  are both integrals, so that  $tF_r(t) g(x_r, t)$  is an integral, and has, moreover, like  $tF_r(t)$ , the unique limit zero, when  $t \to 0$ .

Combining this with (1), we see that A+B+C has limits which differ by as little as we please from those of an expression of the form

$$(\mathbf{L}'\cos px_r + \mathbf{M}'\sin px_r)\csc \frac{1}{2}x_r$$

where

$$\mathbf{L}' = p \int_{-\epsilon}^{\epsilon} \mathbf{F}_{r}(t) \cos pt \, dt - \sin p\epsilon \left[ \mathbf{F}_{r}(\epsilon) + \mathbf{F}_{r}(-\epsilon) \right].$$

and, transforming M in the same way as we transformed L above,

$$\mathbf{M}' = p \int_{-\epsilon}^{\epsilon} \mathbf{F}_{r}(t) \sin pt \, dt + \cos p \left[ \mathbf{F}_{r}(\epsilon) - \mathbf{F}_{r}(-\epsilon) \right].$$

But, by the hypothesis (ii), the expressions L' and M' have limits as small as we please, for all values of r = 1, 2, ..., s. Thus each of the expressions R with which we started has limits as small as we please, which proves the theorem.

Cor.—In condition (iii) p may be replaced by n, without disturbing the validity of the theorem.

As regards the second and third members of the expression, this is almost obvious; in fact, taking, for instance, the sine,

$$F(t+k_r)\sin pt$$

differs from

$$F(t+k_r)\sin nt$$

by 
$$F(t+k_r) \sin nt (1-\cos \frac{1}{2}t) + F(t+k_r) \sin \frac{1}{2}t \cos nt$$
,

which, by the last statement of condition (iii), converges to zero, as  $t \to 0$ , and therefore has, when  $t = \epsilon$ , a value as small as we please.

As regards the integral constituting the first term of the expression, we may clearly replace the p outside the integral by n, since, by the Theorem of Riemann-Lebesgue, we shall only alter the term by a quantity which converges to zero, as n or p becomes infinite. Suppose this change already made. If we now change the p inside the integral into n, we have a difference in value given by the sum of two expressions of the form

$$n\int_{-\epsilon}^{\epsilon} t F(t+k_r) h(t) \int_{sin}^{cos} nt dt$$

where h(t) is an integral. These, by Lemma 1 of § 4, have, for a sufficiently small  $\epsilon$ , limits as small as we please. For  $tF(t+k_r)h(t)$  is an integral which approaches zero, as  $t \to 0$ , and, therefore, as shown in that lemma, integrating by parts, and, using the Theorem of Riemann-Lebesgue, our result follows.

## § 7. We now come to our fundamental auxiliary theorem.

THEOREM IV.—The (ordinary) upper and lower functions of the first derived series of the Fourier series of F(x) at a particular point x (other than the points  $k_1, k_2, ..., k_s$ , to be immediately specified) depend only on the nature of F(t) in a neighbourhood enclosing the point t = x considered, as small as we please, provided the following conditions be satisfied:—

- (i) Except in an interval which contains one at least of a certain finite number of points,  $k_1, k_2, ..., k_s$ , F(t) is an absolutely convergent integral.
- (ii)  $tF(k_r+t)$  is an absolutely convergent integral for r=1, 2, ..., s, in a certain interval containing t=0, and converges to zero, when t+0.
- (iii) If  $q_r(t)$  denote any function which, except in a certain sub-interval of the interval  $(-\pi, \pi)$ , surrounding  $t = k_r$ , is a periodic integral, and in that exceptional sub-interval is equal to F(t), then the coefficients of the derived series of the Fourier series of  $q_r(t)$  converge to zero, for r = 1, 2, ..., s.

For, if the conditions (iii) hold,

$$\lim_{n\to\infty} \frac{n}{\pi} \int_{-\pi}^{\pi} q_r(t) \frac{\cos nt}{\sin nt} dt = 0.$$

Hence

$$\operatorname{Lt}_{n \to \infty} n \int_{-\pi}^{\pi} q_r(t) \frac{\cos n}{\sin n} (t - k_r) dt = 0.$$

Therefore, since  $q_r(t)$  is periodic,

$$\operatorname{Lt}_{n\to\infty} n \int_{-\pi}^{\pi} q_r (t+k_r) \frac{\cos}{\sin n} nt \, dt = 0$$
 (1)

Now

$$n\int_{\epsilon}^{\pi}q_{r}(t+k_{r})\frac{\cos}{\sin nt} dt = \left[q_{r}(t+k_{r})\frac{\sin n}{-\cos nt}\right]_{\epsilon}^{\pi} - \int_{\epsilon}^{\pi}q_{r}(t+k_{r})\frac{\sin n}{-\cos nt} dt,$$

where the integral on the right vanishes when  $n \to \infty$ , by the Theorem of Riemann-Lebesgue. Hence, as  $n \to \infty$ ,

$$n\int_{\epsilon}^{\pi}q_{r}(t+k_{r})\frac{\cos nt\,dt-q_{r}(\pi+k_{r})\sin n\pi+q_{r}(\epsilon+k_{r})\sin n\epsilon\to 0. \tag{2}$$

In like manner

$$n \int_{-\pi}^{-\epsilon} q_r (t+k_r) \frac{\cos n}{\sin nt} dt - q_r (-\epsilon + k_r) \frac{-\sin n}{\cos n\epsilon} n\epsilon + q_r (-\pi + k_r) \frac{-\sin n}{\cos n\tau} n\pi + 0. \quad (3)$$

Also 
$$n \int_{-\epsilon}^{\epsilon} q_r(t+k_r) \frac{\cos}{\sin nt} dt = n \int_{-\epsilon}^{\epsilon} \mathbf{F}(t+k_r) \frac{\sin}{\cos nt} dt. \tag{4}$$

Adding (2), (3) and (4), and comparing with (1), we get, finally,

$$\left\{n\int_{-\epsilon}^{\epsilon} \mathbf{F}(t+k_r) \frac{\cos n}{\sin n} nt - \left[q\mathbf{F}_r(\epsilon+k_r) \pm q\mathbf{F}_r(-\epsilon+k_r)\right] \frac{\cos n}{\sin n} \epsilon\right\} \to 0, \quad (5)$$

since 
$$\sin n\pi = 0$$
, and  $q_r(\pi + k_r) = q_r(-\pi + k_r)$ , and  $q_r(\epsilon + k_r) = F(\epsilon + k_r)$ ,  $q_r(-\epsilon + k_r) = F(-\epsilon + k_r)$ .

Now, as in the preceding corollary, we may in (5) replace n by p, where  $p = n + \frac{1}{2}$ . The conditions (i), (ii), and (iii) of Theorem III of § 6 are therefore satisfied. Hence, by Theorems II and III,

Lt 
$$I_n = \operatorname{Lt}_{n \to \infty} \frac{d}{dx} \int_{c}^{\pi} [F(x+u) + F(x-u)] \sin(n+\frac{1}{2}) u \operatorname{cosec} \frac{1}{2} u \, du = 0.$$

This, by Theorem I, proves the theorem.

§ 8. From Theorem IV of the preceding article, we conclude easily that whole classes of restricted Fourier series of the kind contemplated actually exist. In a recent communication to the Society, I have virtually obtained sufficient conditions for the fulfilment of condition (iii) of Theorem IV above. We proceed first to show that these sufficient conditions ensure at the same time the fulfilment of condition (ii).

Lemma 3.—If F(u) is an integral in every interval not containing the origin, and if any one of the following conditions holds in some interval containing the origin,

(i) 
$$u F'(u)$$
 is bounded;

(ii) 
$$F(u) - \frac{1}{u} \int_{0}^{u} F(u) du \text{ is an integral;}$$

(iii) 
$$u^2F''(u)$$
 is bounded;

then uF(u) is an integral in the whole interval of periodicity, and approaches zero when  $u \to 0$ .

We have, in fact, if G(u) is the integral of F(u),

$$\frac{d}{du}[u\mathbf{F}(u)] = \mathbf{F}(u) + u\mathbf{F}'(u) = \frac{d}{du}\mathbf{G}(u) + u\mathbf{F}'(u),$$

and, therefore, in case (i), the differential coefficient of uF(u)-G(u) is bounded, so that uF(u)-G(u) is an integral, and, therefore, uF(u) is an integral, which, by the theory of indeterminate forms, has the same limit as  $-u^2F'(u)$ , that is zero.

In case (ii), if we multiply by u, we still get an integral, which accordingly approaches zero, when  $u \to 0$ , hence the required result follows.

In case (iii), we remark that, by the theory of indeterminate forms,

has its limits among those of

$$F''(u)/(-1/u^2)$$
,

so that (iii) becomes a special case of (i).

§ 9. We now give the conditions alluded to in the previous article, which

ensure simultaneously the holding of the conditions (ii) and (iii) of Theorem IV. Taken in conjunction with that theorem, they give us the main results of the paper, stated in the Introduction.

**THEOREM A.**—The conditions (ii) and (iii) of Theorem IV are satisfied, for a particular value of r if, for that value of r, we have, as  $u \to 0$ ,

(a) 
$$\mathbf{F}(k_r+u) - \mathbf{F}(k_r-u) \to 0 \; ; \; and$$

(b) 
$$u \frac{d}{du} \left[ \mathbf{F} \left( k_r + u \right) + \mathbf{F} \left( k_r - u \right) \right] \to 0 ;$$

and if further

(v)  $u\mathbf{F}'(k_r+u) = uf(k_r+u)$  is for some interval surrounding u=0, a function of bounded variation;

or, more generally, if we have, in addition to (a), the following:-

(b') 
$$\frac{1}{u} \int_{0}^{u} t \left[ f(t+k_{r}) - f(k_{r}-t) \right] dt \to 0, \text{ when } u \to 0;$$

(c') 
$$F(u+k_r) - \frac{1}{u} \int_0^u F(t+k_r) dt$$
 is an integral for an interval containing  $u=0$ .

Condition (a) secures that the odd function  $F(k_r+u)-F(k_r-u)$  has zero as limit, when  $u \to 0$ , and (c) secures that u times the differential coefficient of the same odd function is a function of bounded variation. Hence we may apply Theorem 4 of my paper cited above, and deduce the convergence to zero of the coefficients of the derived series of the extended odd function, which is elsewhere an integral, and in the given small interval agrees with the above odd function.

Similarly conditions (b) and (c) secure that u times the differential coefficient of the even function  $F(k_r+u)+F(k_r-u)$  is a function of bounded variation, which converges to zero, as  $u \to 0$ . Thus by Theorem 3 of the same paper, the coefficients of the derived series of the extended even function converge to zero.

Hence the coefficients both of the cosine and the sine terms of the derived series of the Fourier series of a function which is equal to F(u) in the given small interval containing  $u = k_r$ , and is elsewhere an integral, converge to zero. Hence condition (iii) of Theorem IV is satisfied.

With regard to condition (ii), this is, by Lemma 3, satisfied, as by condition (c) of the present theorem  $uF'(k_r+u)$  is bounded.

This proves the theorem when (a), (b), and (c) are satisfied.

To see that (b') and (c') may take the place of (b) and (c), we remark first that, by Lemma 3,  $uF(u+k_r) = uF_r(u)$  approaches zero, as  $u \to 0$ , and that, therefore, from the equation

$$\int_{\epsilon}^{u} u f_{r}(u) du = u F_{r}(u) - \int_{\epsilon}^{u} F_{r}(u) du - F_{r}(\epsilon),$$

we may deduce that

$$\int_0^u u f_r(u) du = u F_r(u) - \int_0^u F_r(u) du,$$

and, therefore, that the left-hand side of the last equation, being the difference of two integrals, is an ordinary Lebesgue integral.

Moreover we see that

$$\frac{1}{u}\int_{0}^{u}uf(u)\,du$$

is itself an ordinary Lebesgue integral.

The rest of the argument is precisely analogous to that employed in dealing with the set of conditions (a), (b), and (c) except that, instead of using Theorems 3 and 4 of the paper cited as basis, we now use the more general Theorems 5 and 6 of that same paper.

§ 10. The following theorem is based on Theorems 7 and 8 of the paper previously cited, and in its most general form, on a slight generalisation of the result of my 'Comptes Rendus' paper, there utilised.

THEOREM B.—Retaining conditions (a) of Theorem A, we may replace (b) and (c) by the following:—

(b")  $u^2\mathbf{F}'(u+k_r)$  is bounded in some interval surrounding u=0, and  $u\mathbf{F}'(u+k_r)$  has a unique limit as  $u\to 0$ ,  $\mathbf{F}''$  denoting a derivate of  $\mathbf{F}'$ .

In fact, by Lemma 3, condition (ii) of Theorem IV is satisfied.

More generally we may replace (b) and (c) by the following:-

(b''')  $\frac{1}{u} \int \left| d(t^2 \mathbf{F}'(t+k_r)) \right|$  is bounded in some interval surrounding u = 0, and  $u\mathbf{F}'(u+k_r)$  has a unique limit, as  $u \to 0$ .

In fact, by Lemma 3, condition (ii) of Theorem IV is satisfied. Also considering (c''), if we write

$$g(u) = \frac{d}{du} [u^2 \mathbf{F}'(u + k_r)] = 2u f(k_r) + u^2 f'(u + k_r),$$

we see that y(u) is bounded, say numerically less than B.

Further

$$uf(u+k_r) = \frac{1}{u} \int_0^u g(t) dt,$$

where

$$\frac{1}{u} \int_{0}^{u} g(t) dt \leq B,$$

and is accordingly bounded.

We can accordingly employ Theorems 7 and 8 of the paper already cited, and the required result follows.

To prove the remaining part of the theorem, we have merely to use the condition that

$$\frac{1}{u} \int_{0}^{u} \left| du \left[ \phi \left( x+u \right) + \phi \left( x-u \right) \right] \right|$$

should be bounded, instead of the slightly less general condition that

$$\frac{1}{u} \int_0^u \frac{d}{du} u \left[ \varphi(x+u) + \varphi(x-u) \right] du$$

in the test for the convergence of the Fourier series of a function  $\phi(u)$  and of its allied series, quoted in the paper cited from the 'Comptes Rendus.'\*

§ 11. In the Theorems II-IV we have had in view convergence at a point only. That the convergence is uniform, or, more generally, that the quantities have limits which are bounded functions of x, is immediate. Thus we have the following theorem:—

Theorem V.—The expression 
$$\frac{d}{dx} \int_{e}^{\pi} [F(x+u) + F(x-u)] \sin pu \csc \frac{1}{2} u \, du \, of$$

Theorem I converges uniformly to zero in any closed interval internal to a completely open interval, in which the conditions of Theorem IV hold.

We have, in fact, only to examine the proofs of Theorems II, III, and IV to see firstly that, for such a closed interval, there is a finite upper and a finite lower bound to each of the factors which involve x, e.g.

$$\cos p(x-\alpha-t)$$
 cosec  $\frac{1}{2}(x-\alpha-t)$ ,

or  $g(x, \epsilon)$  in Theorem III; and, secondly, that wherever the Theorem of Riemann-Lebesgue is used, the convergence is, by a known property of the integral in question, uniform convergence to zero for values of x in our closed interval. Finally, where the argument introduces a small quantity  $\epsilon$ , which, when chosen conveniently small, ensures certain auxiliary quantities being as small as we please, we see that these auxiliary quantities may be made less than an assigned small quantity independent of x, since, x being a point of a closed interval inside a completely open interval in which the conditions hold,  $\epsilon$  may be chosen independent of x, and, by the point first referred to, the auxiliary quantity in question may be made to depend only on  $\epsilon$ . Thus the theorem is proved.

§ 12. Referring then to Cor. 2 of Theorem I, we at once obtain the following results in the theory of term-by-term integration of restricted Fourier series when multiplied by another function:—

THEOREM C.—If f(x) is a function which in a certain sub-interval of the

<sup>\*</sup> The proof of the extended form of test is almost exactly the same as that given in the 'Comptes Rendus.' It is given in extense in a paper on "The Convergence of the Derived Series of a Fourier Series," cited above.

interval of periodicity has its square summable, and a(x) is another function whose square is summable, then, if we multiply the restricted Fourier series of f(x) by g(x), we may integrate term by term over the sub-interval, and the result will be the integral of the product f(x) g(x) over the same interval, provided only that-

- (i) the restricted nature of the series is due to a finite number of points at which the primitive function F(x) of which f(x) is a derivate is not an integral;
  - (ii) at such points  $k_r$ , (r = 1, 2, ..., s),  $(x-k_r) F(x)$  is an integral;
- (iii) if q denote any function which, except in a certain sub-interval of the interval  $(-\pi, \pi)$  surrounding  $x = k_r$ , is a periodic integral, and in that exceptional sub-interval is equal to F(x), then the coefficients of the derived series of the Fourier series of  $q_r(x)$  converge to zero for r=1, 2, ..., s.

THEOREM D.—If f(x) is a function which, in a certain sub-interval of the interval of periodicity has bounded variation, and g(x) is summable, then, if we multiply the restricted Fourier series of f(x) by g(x), and integrate term by term over the sub-interval, the result will be the integral of the product f(x) g(x) over the same sub-interval, provided only the same conditions hold as in Theorem C.

**THEOREM E.**—If g(x) is any function of bounded variation, then, if we multiply the restricted Fourier series of any function f(x) by g(x), we may integrate term by term over the sub-interval\* to which it is restricted, and the result will be the integral of the product f(x) g(x) over the same sub-interval, provided only the same conditions hold as in Theorem C.

In these theorems, as elsewhere, the integration is supposed to be over a closed interval. By the term therefore "integration over the sub-interval," which is itself necessarily open, we mean that we may integrate between any two points of that open interval.

We may, of course, substitute for the conditions (i), (ii), (iii) any of those sets of conditions stated in Theorems A and B as sufficient to ensure their fulfilment.

It should be noticed that in Theorem D we use the fact that the convergence of the restricted Fourier series in an interval to which it is restricted is necessarily bounded, being of the same character as that for a proper Fourier series, in virtue of Cor. 2 to Theorem I.

\* In the present communication, as in the paper which preceded it, I have confined my attention to first derived series of Fourier series. It is open to us also to consider the circumstances under which the coefficients of the second or higher derived series converge to zero, while the series themselves converge at isolated points, or throughout intervals. No new principles are introduced into the consideration of such higher derived series; I have therefore, thought it undesirable to extend the length of my communications by dealing with them.

## On the Deflection of the Vertical by Tidal Loading of the Earth's Surface.

By Horace Lamb, F.R.S.

(Received January 25, 1917.)

The earliest calculations on the above subject in which the flexure of the earth's surface is taken into account, as well as the direct attraction of the water, are contained in a well known paper by G. H. Darwin.\* It was there shown, in a particular case, that the tilting effect would conspire with the attraction, and would on certain assumptions be directly proportional to it. The latter remark was stated as due originally (in a more general form) to Sir W. Thomson. On inserting numerical values it was found that the apparent deflection due to tilting would considerably exceed that due to attraction.† The whole subject has of late excited renewed attention, owing to its bearing on observations of lunar deflection of gravity,‡ and in a recent paper by Terazawa§ the matter is specially considered from the latter point of view.

The present paper, after discussing a few typical problems, goes on (in § 4) to examine the effect of one or two considerations which have hitherto been disregarded in such calculations. It is true that the corrections involved are under some conditions negligible, but they are of theoretic interest, and it is found that at great distances from a load, and therefore in all cases of widely distributed load, they may attain considerable relative importance. In the first place, owing to the deformation of the earth's surface and the altered distribution of density an additional horizontal component of force on the plumb-line is introduced; this tends to counteract the attraction of the water. A more important point is that the influence of gravity on the deformation has been ignored. In attempting to estimate the effect of gravity it has been found convenient, in order to avoid difficulties not altogether of a mathematical kind, to limit the investigation to the case of incompressibility. I have also neglected, in the first instance, the disturbance in the field of gravity itself, due to the load and the deformation, so far as this affects the strains. When subsequently the alteration of the

<sup>\* &#</sup>x27;Brit. Ass. Reports,' 1882; 'Scientific Papers,' vol. 1, p. 444.

<sup>†</sup> The relation was pointed out independently by Chree, 'Phil. Mag.' (5), vol. 43, p. 177 (1896).

<sup>‡</sup> Love, 'Some Problems of Geodynamics,' p. 88 (1911).

<sup>§ &</sup>quot;On Periodic Disturbance of Level Arising from the Load of Neighbouring Oceanic Tides," 'Phil. Trans.,' A, vol. 217, p. 35 (1916).

field is taken into account a curious point arises. For mathematical simplicity the "earth" has been treated, as is usual in such investigations, as flat and infinitely extended. It appears that if this were the case the surface would be unstable, whatever the degree of rigidity, for disturbances exceeding a certain critical wave-length. This wave-length is, however, enormous, and reason is given for the view that inferences can still legitimately be drawn from our results as to the character of the effects actually produced.

1. For the present purpose, the earth is regarded as a semi-infinite isotropic elastic solid, extending indefinitely on the lower, positive, side of the plane z = 0. If a load of surface density

$$\sigma = J_0(mr), \tag{1}$$

where  $r_1 = \sqrt{(x^2 + y^2)}$ , denotes distance from the origin, be placed upon it, the usual theory, in which elasticity only is taken into account, gives a surface depression

$$w_0 = \frac{(1-\eta)g}{\mu} \cdot \frac{J_0(mr)}{m},$$
 (2)

and a dilatation

$$\Delta = -\frac{g(1-2\eta)}{\mu} e^{-mx} J_0(mr), \tag{3}$$

where  $\mu$  denotes the rigidity, and  $\eta$  Poisson's ratio.\*

The gravitation potential due to the load (1) is

$$V = 2\pi\gamma \frac{e^{\mp mz} J_0(mr)}{m},\tag{4}$$

where  $\gamma$  is the gravitation constant, and the upper or lower sign in the index is to be taken according as z is positive or negative. For the two values of V satisfy Laplace's equation  $\nabla^2 V = 0$ ; they are continuous at the surface; and they give the proper discontinuity in the value of  $\partial V/\partial z$ . The surface potential is therefore

$$V_0 = 2\pi\gamma \frac{J_0(mr)}{m}.$$
 (5)

The apparent deflection of the plumb-line due to tilting is  $-dw_0/dr$ , and the deflection due to the attraction of the load is  $-dV_0/gdx$ . The ratio of the latter to the former is

$$\frac{2\pi\gamma\mu}{(1-\eta)g^2} = \frac{3}{2(1-\eta)} \cdot \frac{\mu/\bar{\rho}}{gR},\tag{6}$$

where R denotes the radius, and  $\bar{\rho}$  the mean density, of the earth. Since this ratio is constant and independent of m, we infer that it is the same for

\* 'Proc. Lond. Math. Soc.,' vol. 34, p. 278 (1902). The formulæ are slightly simplified by the use of  $\eta_1 = \frac{1}{2}\lambda/(\lambda + \mu)$ , in place of  $\lambda$ .

all symmetrical distributions of load, and therefore for a concentrated load, and therefore for all distributions whatever. This verifies Thomson's remark already referred to. If we take for numerical illustration\*

$$\eta = \frac{1}{2}$$
,  $\mu = 4 \times 10^{11}$ ,  $g = 981$ ,  $\gamma = 6.66 \times 10^{-8}$ 

in C.G.S. units, we find

$$\frac{2\pi\gamma\mu}{(1-\eta)g^2} = 0.232. (7)$$

In the case of incompressibility  $(\eta = \frac{1}{2})$  we have, with the above value of  $\mu$ ,

$$\frac{4\pi\gamma\mu}{g^2} = 0.348. \tag{8}$$

The method of passing from (1) to the case of any symmetrical distribution of load is explained in the paper referred to. To deduce the effect of a concentrated load M at the origin we multiply the various expressions by  $Mmdm/2\pi$ , and integrate from m=0 to  $m=\infty$ . Since, however, the deflection due to the attraction of M is  $\gamma M/gr^2$  we have at once

$$-\frac{dw_0}{dr} = \frac{(1-\eta)g}{2\pi\mu} \cdot \frac{M}{r^2},\tag{9}$$

in virtue of the proportionality referred to.

2. In a case specially discussed by Terazawa the load is supposed to be distributed uniformly over a circular area. This can be treated very simply with the help of a formula given by Ferrers.† He proves (in effect) that the potential of a circular disc of radius a and surface density

$$\sigma = \left(1 - \frac{r^2}{a^2}\right)^n,\tag{10}$$

at external points in its plane is

$$\Omega_0 = \frac{\Gamma(\frac{1}{2})\Gamma(n+1)}{\Gamma(n+\frac{3}{2})} a^2 \int_0^{\infty} \left(1 - \frac{r^2}{a^2 + \lambda}\right)^{n+\frac{1}{2}} \frac{d\lambda}{(a^2 + \lambda)\sqrt{\lambda}},\tag{11}$$

the lower limit of integration being  $r^2-a^2$ .

In the present case we have n = 0.4 Putting  $\alpha^2 + \lambda = r^2/\sin^2\theta$ , we find

$$\Omega_0 = 4a^2 \int_0^{4\pi} \frac{\cos^2\theta \, d\theta}{\sqrt{(r^2 - a^2 \sin^2\theta)}} = \frac{4a}{k} \left\{ E_1 - (1 - k^2) \, F_1 \right\},\tag{12}$$

\* It is very uncertain what are the best representative values to take for  $\mu$  and  $\rho$  (the density), on account of the actual variation with depth. If we put  $\rho = 2.5$  the above value of  $\mu$  makes the velocity of propagation of transverse vibrations agree with the value found by seismologists for the upper strata, viz., 4 km. per second.

† "On the Potentials of Ellipsoids . . . of Variable Densities," 'Quart. Journ. Math.,' vol. 14, p. 1.

‡ In the case  $n = \frac{1}{2}$ , also treated in a different manner by Terazawa, the integral reduces; thus

$$\mathbf{Q}_0 = \pi a \left\{ \left( 1 - \frac{1}{2} \frac{r^2}{a^2} \right) \sin^{-1} \frac{a}{r} + \frac{1}{2} \sqrt{\left( \frac{r^2}{a^2} - 1 \right)} \right\}.$$

in the notation of elliptic integrals, the modulus being

$$k = a/r. (13)$$

For the attraction we derive the simple expression

$$-\frac{d\Omega_0}{dr} = 4(F_1 - E_1). \tag{14}$$

Tables of F<sub>1</sub> and E<sub>1</sub>, abridged from Legendre's, are included in several modern collections.

The object of Terazawa's paper was to form some estimate of the possible effect of the periodic tidal loading and unloading of the Atlantic area on Michelson's observations of lunar deflection of gravity at Chicago. The radius of the circle was taken as 2000 km., and the distance of the point at which the effect is to be estimated as 3000 km. If we put  $k = \frac{2}{3}$  we find from (14) on reference to the Tables

$$-\frac{d\Omega_0}{dr} = 1.727. (15)$$

To find the deflection of the pendulum by attraction we must multiply this by  $\gamma \rho_1 h/g$ , where  $\rho_1$  is the density of the water, and h the tidal elevation. Assuming  $\rho_1 = 1$ , h = 100, we find

$$-\frac{dV_0}{qdr} = 1.17 \times 10^{-8},\tag{16}$$

which is Terazawa's result, obtained by a different process. The tilting effect, obtained by multiplying by 4.31, is  $5.04 \times 10^{-8}$ .

Since tidal elevation in one part of the ocean is compensated by depression elsewhere, it may be worth while to notice the case where the tidal elevation in a circular basin is supposed to vary as the distance from a nodal line (x = 0). It follows from another formula of Ferrers that the potential, at points in its plane, of a disc whose surface density is x/a, is

$$\Omega_0' = 2 a^3 x \int_0^{\infty} \left( 1 - \frac{r^2}{a^2 + \lambda} \right)^{\frac{1}{2}} \frac{d\lambda}{(a^2 + \lambda)^2 \sqrt{\lambda}}, \tag{17}$$

the lower limit being  $r^2-a^2$ . If we put  $x=r\cos\phi$ , this is equivalent to

$$\Omega_0' = \frac{4 a^3}{r} \cos \phi \int_0^{4\pi} \frac{\sin^2 \theta \cos^2 \theta \, d\theta}{\sqrt{(r^2 - a^3 \sin^2 \theta)}}, 
= \frac{4}{3} \frac{a \cos \phi}{k^3} \left\{ (2 - k^2) \, \mathbf{E}_1 - 2 \, (1 - k^2) \, \mathbf{F}_1 \right\}, \tag{18}$$

where k = a/r as before. From this we find

$$-\frac{\partial\Omega_0'}{\partial r} = \frac{4}{3}\frac{\cos\phi}{k} \left\{ 4(F_1 - E_1) - k^2(E_1 + F_1) \right\}. \tag{19}$$

If the height of the water be hx/a, the radial deviation of the plumb-line due to attraction is found by multiplication by  $\gamma \rho_1 h/g$ . If  $\rho_1 = 1$ , h = 100,  $k = \frac{2}{3}$ , I find

$$-\frac{\partial V_0}{\partial \partial r} = 3.11\cos\phi \times 10^{-9}.$$
 (20)

The tilting effect is therefore, on the previous assumptions,

$$-\frac{\partial w_0}{\partial r} = 1.34\cos\phi \times 10^{-8}.$$
 (21)

3. Two-dimensional problems of the above kinds can be treated ablinitio by a simpler analysis, but we may conveniently use the result contained in (9). The loads are now supposed applied on infinitely long bands of the surface, parallel (say) to the axis of y. Unless the total load (positive and negative) is zero, the integrals which give the surface depression and the potential are divergent; but we may still draw inferences as to the deflections produced by bands of great length at distances small compared with the length.

Thus, for a linear load of amount M' per unit length, we have

$$-\frac{dV_0}{gdx} = \frac{2\gamma M'}{x},\tag{22}$$

by the theory of the attraction of an infinite straight line, and therefore

$$-\frac{dw_0}{dx} = \frac{(1-\eta)g}{\pi\mu} \cdot \frac{\mathbf{M}'}{x}.$$
 (23)

If we imagine a band of breadth 2a to carry a uniform load  $\rho_1 h$  per unit area, we have for x > a

$$-\frac{d\nabla_0}{adx} = \frac{2\gamma\rho_1h}{a}\log\frac{x+a}{x-a},\tag{24}$$

whence the value of  $-dw_0/dx$  follows as before.

A more interesting case is where the load varies as the distance, positive or negative, from the medial line x = 0. For the sake of comparison with a problem discussed by Darwin,\* the depression within the band, as well as at external points, is considered. The load per unit area being  $\rho_1 hx/a$ , for  $x^2 < a^2$ , we find from (23)

$$\frac{dw_0}{dx} = -\frac{(1-\eta)g\rho_1 h}{\pi\mu a} \int_{-a}^a \frac{x'dx'}{x-x'},\tag{25}$$

If x > a this gives

$$\frac{dw_0}{dx} = -\frac{(1-\eta)g\rho_1h}{\pi\mu} \left(\frac{x}{a}\log\frac{x+a}{x-a}-2\right). \tag{26}$$

For 0 < x < a we have, taking the "principal value" of the integral in (25),

$$\frac{dw_0}{dx} = -\frac{(1-\eta)g\rho_1 h}{\pi\mu} \left(\frac{x}{a} \log \frac{a+x}{a-x} - 2\right). \tag{27}$$

Hence, for x > a,

$$w_0 := \frac{(1-\eta)g\rho_1 ha}{\pi \mu} \left( \frac{x}{a} - \frac{x^2 - a^2}{2a^2} \log \frac{x+a}{x-a} \right); \tag{28}$$

and, for 0 < x < a,

$$w_0 = \frac{(1-\eta)g_1\rho ha}{\pi\mu} \left(\frac{x}{a} + \frac{a^2 - x^2}{2a^2} \log \frac{a+x}{a-x}\right). \tag{29}$$

The arbitrary constants of integration have been adjusted so as to make  $w_0$  vanish for  $x = \infty$ , and to establish continuity at the edge x = a. Since  $w_0$  must be an odd function, the above expressions will hold also for x negative. The graph of  $w_0$  is shown in the figure.



The tilting effect at external points is given by (26); from this the direct attraction of the load can be deduced.

4. Besides the direct attraction of the load on the pendulum there will be a horizontal force due to the changed configuration of the solid earth. If we assume the formulæ (2) and (3) for the deformation, the corresponding potential is found to be

$$-\frac{\pi\gamma\rho}{\mu}\cdot\frac{J_0(mr)}{m^2},\tag{30}$$

which gives in the case of a concentrated load a deflection

$$-\frac{\gamma\rho}{2\mu}\cdot\frac{M}{r}.\tag{31}$$

The effect on the plumb-line is therefore equivalent to a repulsion varying as the inverse distance, whereas the attraction of the load varies as the inverse square. It is not worth while to give the proof of the formulæ, for the effect could only become appreciable at very great distances from the load, and in these regions the deformation, which has been assumed to be given by (2), is seriously affected by the action of gravity, which is next to be considered. The effect here referred to is included implicitly in the amended results.

5. When we proceed to examine the effect of gravity in modifying the deformations, we are met by difficulties relating to the state of initial stress of the earth. To avoid these the material is here assumed to be incompressible, and the initial stress to consist of a uniform hydrostatic pressure.

$$p_1 = g\rho z. (32)$$

\* Cf. Rayleigh, "On the Dilatational Stability of the Earth," 'Roy. Soc. Proc.,' A, vol. 77, p. 486 (1906); 'Scientific Papers,' vol. 5, p. 300.

It is also assumed for the present that in calculating the strains we may neglect the alteration in the distribution of gravity due to them and to the load.

It is convenient to begin with the two-dimensional case. On the above hypothesis the elastic equations are, in the usual notation,

$$\mu \left( \frac{\partial^2 u}{\partial x^3} + \frac{\partial^2 u}{\partial z^3} \right) = \frac{\partial p}{\partial x}$$

$$\mu \left( \frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial z^2} \right) = \frac{\partial p}{\partial z}$$
(33)

where p denotes the excess of pressure over its initial value  $p_1$ . Assuming for a typical solution,

$$p = Ce^{-mz}\cos mx, \tag{34}$$

we have

$$u = \frac{C}{2\mu} (z + A) e^{-mz} \sin mx$$

$$w = \frac{C}{2\mu} (z + B) e^{-mz} \cos mx$$
(35)

The condition of incompressibility, viz.

$$\frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} = 0, \tag{36}$$

gives

$$A - B = -\frac{1}{m}, \tag{37}$$

whilst the condition of vanishing tangential stress, viz.

$$\frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} = 0, \tag{38}$$

at the surface z = 0, gives

$$A + B = \frac{1}{m}. (39)$$

Hence A = 0, B = 1/m, so that

$$w = \frac{C}{2\mu m} mz e^{-mz} \sin mx$$

$$w = \frac{C}{2\mu m} (1 + mz) e^{-mz} \cos mx$$

$$(40)$$

It may be noticed that  $\partial w/\partial z$  vanishes at the surface.

If  $\sigma$  be the surface-density of the load, the surface condition is

$$-p_1 - p + 2\mu \frac{\partial w}{\partial z} = -g\sigma, \tag{41}$$

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to be satisfied for  $z = w_0$ . Since  $\partial p_1/\partial z = g\rho$ , this becomes

$$g\rho w_0 + p - 2\mu \frac{\partial w}{\partial z} = g\sigma, \tag{42}$$

to be satisfied for z = 0. Hence if

$$\sigma = H \cos mx \tag{43}$$

we have

$$\left(1 + \frac{g\rho}{2\,\mu m}\right)C = gH. \tag{44}$$

Thus

$$w_0 = \frac{g\mathbf{H}}{2\,\mu} \cdot \frac{\cos mx}{m+\kappa},\tag{45}$$

where

$$\kappa = g\rho/2\mu. \tag{46}$$

To deduce the effect of a concentrated load of line-density M' we put  $H = M' dm/\pi$ , and integrate from 0 to  $\infty$ . Thus

$$w_0 = \frac{M'g}{2\pi\mu} \int_0^{\infty} \frac{\cos mx}{m+\kappa} dm = \frac{Mg}{2\pi\mu} \int_0^{\infty} \frac{me^{-mx}}{m^2 + \kappa^2} dm, \tag{47}$$

or

$$w_0 = \frac{\mathbf{M}'g}{2\pi\mu} \left\{ \left( \frac{1}{2}\pi - \operatorname{Si} \kappa x \right) \sin \kappa x - \operatorname{Ci} \kappa x \cos \kappa x \right\}, \tag{48}$$

in the ordinary notation of the sine- and cosine-integrals, viz.

Si 
$$x = \int_0^x \frac{\sin x}{x} dx$$
, Ci  $x = -\int_x^\infty \frac{\cos x}{x} dx$ . (49)

We may notice that the value of  $w_0$  is now finite except for x = 0. From (48) we deduce

$$-\frac{dw_0}{dx} = \frac{\mathbf{M}'g}{2\pi\mu} \left\{ \frac{1}{x} - \kappa \left( \frac{1}{2}\pi - \operatorname{Si}\kappa x \right) \cos \kappa x - \kappa \operatorname{Ci}\kappa x \sin \kappa x \right\}, \tag{50}$$

which now takes the place of (23).

As regards the numerical value of  $\kappa$  we have, taking  $\mu/\rho = 16 \times 10^{10}$ ,

$$\kappa^{-1} = 3260 \text{ km}.$$
 (51)

In any practical application we are therefore concerned only with moderate values of  $\kappa x$ .

The following table gives in Column I values of the function

$$\int_{0}^{\infty} \frac{\sin mx}{m+\kappa} dm = (\frac{1}{2}\pi - \operatorname{Si}\kappa x) \cos \kappa x + \operatorname{Ci}\kappa x \cos \kappa x, \tag{52}$$

based on Glaisher's tablest of the standard integrals (49). In Column II

- \* As to the equality of the two integrals, see the author's 'Hydrodynamics' (1916), Art. 243, where other references are given.
- † 'Phil. Trans.,' p. 367 (1870). An abstract is given in Dale's 'Five-Figure Tables of Mathematical Functions,' London, 1903.

this function is multiplied by  $\kappa x$ , and the result subtracted from unity. This shows the ratio in which the tilting effect is diminished from its value as given by the formula (23), where gravity was neglected. At small distances the change is slight, but at a distance of 1000 km., for example, the tilting is reduced by the action of gravity to the extent of 30 per cent.

KX.	r.	II.	ĸ.v.	I.	II.
0.0	00	1 0	0.5	0 -8605	0 · 570
0.05	1 ·3980 1 ·2910	0 ·980 0 ·871	0.6	0 ·7985 0 ·7451	0 .521
0.5	1 .1869	0.778	0.8	0.6987	0.441
0.8	1 .0286	0.698	0.9	0.6578	0.408
0.4	0 .9341	0.626	1.0	0.6214	0.879

It is to be remarked that on the present suppositions the residual horizontal attraction on the pendulum, when allowance is made for the altered attraction of the solid, bears the same constant ratio to the tilting effect as in Art. 1 above. Recurring to the distribution (43), and assuming for the potential due to the load and to the change of configuration of the solid

$$V = De^{\mp mz} \cos mx, \tag{53}$$

we have, on account of the discontinuity in  $\partial V/\partial z$ ,

$$2mD\cos mx = 4\pi\gamma(\sigma - \rho w_0), \qquad (54)$$

$$D = \frac{2\pi\gamma H}{m+\kappa}.$$
 (55)

$$\frac{V_0}{gw_0} = \frac{4\pi\gamma\mu}{g^2}. (56)$$

Since this does not involve m, the ratio will hold for all two-dimensional distributions of load. With the former numerical data its value has been found to be 0.348.

6. A similar investigation can be made for the case of a load concentrated at a point. The elastic equations are

$$\mu \nabla^2 u = \frac{\partial p}{\partial x}, \qquad \mu \nabla^2 v = \frac{\partial p}{\partial y}, \qquad \mu \nabla^2 w = \frac{\partial p}{\partial z}, \tag{57}$$

$$\nabla^2 p = 0. \tag{58}$$

If q denote radial displacement in a horizontal plane, so that

$$u = qx/r, \qquad v = qy/r, \tag{59}$$

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the equations become, in the case of symmetry about the origin,

$$\mu \left( \frac{\partial^{2} q}{\partial r^{2}} + \frac{1}{r} \frac{\partial q}{\partial r} - \frac{q}{r^{2}} + \frac{\partial^{2} q}{\partial z^{2}} \right) = \frac{\partial p}{\partial r}$$

$$\mu \left( \frac{\partial^{2} w}{\partial r^{2}} + \frac{1}{r} \frac{\partial w}{\partial r} + \frac{\partial^{2} w}{\partial z_{2}} \right) = \frac{\partial p}{\partial z}$$

$$, \tag{60}$$

with

$$\frac{\partial^2 p}{\partial r^2} + \frac{1}{r} \frac{\partial p}{\partial r} + \frac{\partial^2 p}{\partial z^2} = 0. \tag{61}$$

Assuming

$$p = Ce^{-mz}J_0(mr), (62)$$

we find

$$q = \frac{C}{2\mu} (z + A) e^{-mz} J_1(mr)$$

$$w = \frac{C}{2\mu} (z + B) e^{-mz} J_0(mr)$$
(63)

The condition of incompressibility, viz.

$$\frac{\partial q}{\partial r} + \frac{q}{r} + \frac{\partial w}{\partial z} = 0, (64)$$

leads to

$$\mathbf{A} - \mathbf{B} = -\frac{1}{m},\tag{65}$$

whilst the condition of zero tangential stress at the surface, viz.

$$\frac{\partial q}{\partial z} + \frac{\partial w}{\partial r} = 0. ag{66}$$

gives

$$A + B = \frac{1}{m}. (67)$$

Hence A = 0, B = 1/m, so that

$$w = \frac{C}{2\mu m} (1 + mz) e^{-mx} J_0(mr).$$
 (68)

The surface-condition has again the form (42). If the load be

$$\sigma = H J_0(mr) \tag{69}$$

we find

$$w_0 = \frac{gH}{2\mu} \cdot \frac{J_0(mr)}{m+\kappa},\tag{70}$$

where  $\kappa$  has the value (46).

To pass to the case of a concentrated load M at the origin, we put  $H = Mmdm/2\pi$ , and integrate from 0 to  $\infty$ . Thus

$$w_0 = \frac{Mg}{4\pi\mu} \int_0^\infty \frac{mJ_0(mr)}{m+\kappa} dm = \frac{Mg}{4\pi\mu} \left\{ \frac{1}{r} - \kappa \int_0^\infty \frac{J_0(mr)}{m+\kappa} dm \right\}$$
$$= \frac{Mg}{4\pi\mu} \left\{ \frac{1}{r} - \kappa \int_0^\infty e^{-\kappa r \sinh u} du \right\}, (71)^*$$

<sup>\*</sup> A proof of the equality of the two integrals last written is given in the Appendix to this paper.

An asymptotic expansion of the latter integral is easily obtained, but has hardly any application from the present point of view. For moderate values of  $\kappa r$  we have recourse to the formula\*

$$\int_0^\infty e^{-x \sinh u} du = \int_0^{\frac{1}{2}\pi} \sin(x \cos \theta) d\theta + \frac{1}{2}\pi K_0(x), \tag{72}$$

where  $K_0(x)$  is the Bessel's function "of the second kind" defined by

$$\mathbf{K}_{0}(x) = \frac{2}{\pi} \int_{0}^{\infty} \cos(x \cosh u) \, du. \tag{73}$$

Hence

$$\int_0^\infty \frac{J_0(mr)}{m+\kappa} dm = \kappa r - \frac{(\kappa r)^2}{1^2 \cdot 3^2} + \frac{(\kappa r)^5}{1^2 \cdot 3^2 \cdot 5^2} - \dots + \frac{1}{2} \pi K_0(\kappa r). \tag{74}$$

The function  $\frac{1}{2}\pi K_0$  has been tabulated by B. A. Smith; under the designation  $\kappa J_0 - Y_0$ , where  $\kappa$  stands for log 2—C or 0.11593, C being Euler's constant. With this assistance the following Table has been constructed. Column I gives the values of the function (74); in Column II these are multiplied by  $\kappa r$  and subtracted from unity. The result gives the ratio in which the surface depression  $w_0$  is diminished by gravity:—

ĸr.	ī.	II.	Kr.	I.	11.
0.0	<b>x</b> 0	1.0	0.5	1 ·1845	0 .408
0.02	8 ·1591	0.842	0.8	1 .0609	0 .864
0.1	2 5098	0 .749	0.7	0 9621	0.327
0.2	1 8973	0.620	0.8	0 .8807	0 .295
0.8	1 · 5650	0.580	0.9	0.8125	0 .269
0.4	1 .8448	0 462	1.0	0.7541	0.246

The tilting effect is

$$-\frac{dw_0}{dr} = \frac{Mg}{4\pi\mu} \left\{ \frac{1}{r^2} - \kappa \int_0^\infty \frac{mJ_1(mr)}{m+\kappa} dm \right\}. \tag{75}$$

From (74) we have

$$\frac{1}{\kappa} \int_{0}^{\infty} \frac{m J_{1}(mr)}{m + \kappa} dm = \frac{1}{2} \kappa K_{1}(\kappa r) - \left\{ 1 - \frac{(\kappa r)^{3}}{1^{3} \cdot 3} + \frac{(\kappa r)^{4}}{1^{2} \cdot 3^{3} \cdot 5} - \dots \right\}, \quad (76)$$

where  $K_1$  is written for  $-K_0$ . The function  $\frac{1}{2}\pi K_1$  has also been tabulated by Smith under the designation  $\kappa J_1 - Y_1$ . The following Table gives in

<sup>\*</sup> Of. 'Hydrodynamics,' Art. 194.

<sup>†</sup> This formula occurs in Nielsen's 'Handbuch der Cylinderfunktionen,' Leipzig, 1904, p. 238, but the derivation is different. The ascending series occurs in another connection in Rayleigh's 'Theory of Sound,' Art. 302, where it is denoted by  $\frac{1}{2}\pi K_0$ . Nielsen denotes it by  $\frac{1}{2}\pi Z_0$ , and writes  $-Y_0$  for the function on the right-hand side of (73). The notation in the text is employed by H. Weber.

<sup>† &#</sup>x27;Phil. Mag.' (5), vol. 45, p. 122 (1898).

Column I the values of the function in (76); in Column II these are multiplied by  $(\kappa r)^2$  and subtracted from unity. The results show the ratio in which the tilting effect is reduced by gravity:—

I.	II.	ĸr.	I.	II.
00 10:0011	1.0	0.5	1 :8984	0 .652
9 1490	0.908	0.7	0.8914	0 .568
4 2342	0.881	0.8	0.7418	0 .525
				0 490
	19 ·0911 9 ·1490	∞ 1·0   19·0911 0·952   9·1490 0·908   4·2342 0·681   2·6318 0·763	∞ 1 ·0 0 ·5 19 ·0911 0 ·952 0 ·6 9 ·1490 0 ·908 0 ·7 4 ·2242 0 ·881 0 ·8 2 ·6818 0 ·763 0 ·9	∞   1·0   0·5   1·3934     19·0911   0·952   0·6   1·0971     9·1490   0·908   0·7   0·8914     4·2342   0·831   0·8   0·7418     2·6318   0·763   0·9   0·6293

It is easily seen that the residual horizontal attraction will bear to the tilting effect the same constant ratio as in the two-dimensional case of the preceding section.

7. It remains to take into account the fact that the gravitational field is altered by the presence of the load and the deformation of the surface, and that the strains are thereby, to some extent, modified.

Taking first the two-dimensional case, the equations (33) are replaced by

$$\mu \left( \frac{\partial^{2} u}{\partial x^{2}} + \frac{\partial^{2} u}{\partial z^{2}} \right) = \frac{\partial p}{\partial x} - \rho \frac{\partial V}{\partial x}$$

$$\mu \left( \frac{\partial^{2} w}{\partial x^{2}} + \frac{\partial^{2} w}{\partial z^{2}} \right) = \frac{\partial p}{\partial y} - \rho \frac{\partial V}{\partial z}$$
(77)

where V is the potential due to the load and to the change of configuration of the surface. If we assume

$$p = Ce^{-mx}\cos mx \tag{78}$$

as before, and

$$\rho V = C_1 e^{\mp mx} \cos mx, \tag{79}$$

we have, writing  $C-C_1$  for C in (40),

$$w_0 = \frac{\mathbf{C} - \mathbf{C_1}}{2\,\mu m} \cos mx. \qquad . \tag{80}$$

The load being

$$\sigma = H \cos mx, \tag{81}$$

the surface-condition (42) gives

$$\frac{g\rho}{2\,\mu m}(\mathbf{C} - \mathbf{C}_1) + \mathbf{C} = g\mathbf{H}.\tag{82}$$

Since the value of  $\partial V/\partial z$  just above the surface must exceed the value just below by  $4\pi\gamma(\sigma-\rho w_0)$ , we have also

$$\frac{2mC_1}{\rho} = 4\pi\gamma \left\{ H - \frac{\rho (C - C_1)}{2\mu m} \right\}. \tag{83}$$

Vertical by Tidal Loading of the Earth's Surface.

Hence 
$$C_1 = \frac{2\pi\gamma\rho}{g} \cdot \frac{C}{m}$$
, (84)

and 
$$\left(m^2 + \frac{g\rho}{2\mu} m - \frac{\pi \gamma \rho^2}{\mu}\right) C = m^2 g H. \tag{85}$$

Hence, putting

$$m^2 + \frac{g\rho}{2\mu} m - \frac{\pi\gamma\rho^2}{\mu} = (m+\alpha)(m-\beta),$$
 (86)

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we find

$$w_0 = \frac{gH}{2\mu} \cdot \frac{m - \alpha\beta/(\alpha - \beta)}{(m + \alpha)(m - \beta)} \cos m\omega, \tag{87}$$

$$\frac{\mathbf{V}_0}{g} = \frac{2\pi\gamma\mathbf{H}}{g} \cdot \frac{m}{(m+\alpha)(m-\beta)}\cos mx. \tag{88}$$

It appears that for  $m=\beta$  the equilibrium would be neutral; i.e. a deformation of wave-length  $2\pi/\beta$  could subsist independently of any external load. For greater wave-lengths the equilibrium would be unstable. This gravitational instability of an infinitely extended plane surface may be unexpected, but it is easily verified in the case of a plane sheet of water, where  $\mu=0$ . It is evident that in the absence of the earth's attraction and of rigidity the mass would tend to cumulate. The introduction of ordinary gravity, and even of rigidity, merely imposes a lower limit to the wave-length at which instability sets in.

This limit is however very high. From (86) we find

$$\alpha = \frac{g\rho}{4\mu} \left\{ \sqrt{\left(1 + \frac{16\pi\gamma\mu}{g^2}\right) + 1} \right\}$$

$$\beta = \frac{g\rho}{4\mu} \left\{ \sqrt{\left(1 + \frac{16\pi\gamma\mu}{g^2}\right) - 1} \right\}$$
(89)

With the previous numerical values of the constants I find

$$\alpha^{-1} = 2560 \text{ km.}, \quad \beta^{-1} = 11,940 \text{ km.},$$
 (90)

whence  $2\pi/\beta = 75,000$  km., or nearly twice the circumference of the earth! This indicates that the paradox has arisen through our ignoring the curvature and restricted dimensions of the earth.

Waiving this difficulty for the moment we have

$$-\frac{dw_0}{dx} = \frac{gH}{2\mu} \left\{ 1 - \frac{1}{\alpha^2 - \beta^2} \left( \frac{\alpha^3}{m + \alpha} + \frac{\beta^3}{m - \beta} \right) \right\} \sin mx, \tag{91}$$

$$-\frac{dV_0}{gdx} = \frac{2\pi\gamma H}{g} \left\{ 1 - \frac{1}{\alpha + \beta} \left( \frac{\alpha^3}{m + \alpha} - \frac{\beta^2}{m - \beta} \right) \right\} \sin mx. \tag{92}$$

\* This is seen most by directly investigating the effect of a surface pressure P cos mx, instead of a material load. We should find

$$w_0 = \frac{P}{2\mu} \cdot \frac{m^2}{(m+a)(m-\beta)} \cos mx,$$

which has the same sign as P, or the opposite, according as  $m \ge \beta$ .

· Hence, for a concentrated linear load,\*

$$-\frac{dw_0}{dx} = \frac{\mathbf{M}'g}{4\pi\mu} \left\{ \frac{1}{x} - \frac{\alpha^3}{\alpha^3 - \beta^3} \int_0^x \frac{\sin mx}{m + \alpha} dm - \frac{\beta^3}{\alpha^3 - \beta^3} \int_0^x \frac{\sin mx}{m - \beta} dm \right\}, \quad (93)$$

$$-\frac{dV_0}{qdx} = \frac{\gamma M'}{q} \left\{ \frac{1}{x} - \frac{\alpha^2}{\alpha + \beta} \int_0^\infty \frac{\sin mx}{m + \alpha} dm + \frac{\beta^2}{\alpha + \beta} \int_0^\infty \frac{\sin mx}{m - \beta} dm \right\}. \tag{94}$$

The second definite integral in these expressions is indeterminate to the extent of additive terms of the form

A cos 
$$\beta x + B \sin \beta x$$
.

Its "principal value" is

$$P\int_{0}^{\infty} \frac{\sin mx}{m-\beta} dm = \pi \cos \beta x - \int_{0}^{\infty} \frac{\sin mx}{m+\beta} dm$$
$$= (\frac{1}{2}\pi + \operatorname{Si}\beta x) \cos \beta x - \operatorname{Ci}\beta x \sin \beta x. \tag{95}$$

The adoption of the principal value of an indeterminate integral may appear somewhat arbitrary, and it may be questioned whether results obtained in this way have any physical significance. The consideration of the following modified problem may perhaps serve to justify the procedure.

Suppose that we have an endless series of alternately positive and negative loads  $\pm M'$  at the points  $x = 0, \pm \alpha, \pm 2\alpha,...$  These may be represented as the limit when  $h \to 1$  of

$$\sigma = \frac{\mathbf{M}'}{a} \left( h \cos \frac{\pi x}{a} + h^3 \cos \frac{3\pi x}{a} + h^5 \cos \frac{5\pi x}{a} + \dots \right) \tag{96}$$

For, summing the series, we have

$$\sigma = \frac{M'h}{a} \cdot \frac{1 - h^2}{1 - 2h^2 \cos \frac{2\pi x}{a} + h^4},\tag{97}$$

the limit of which is zero, except when x is zero or a multiple of  $\pm a$ . Also, if b < a we have

$$\int_{-b}^{b} \sigma dx = \frac{2M'}{\pi} \tan^{-1} \left\{ \frac{2h \sin(\pi b/a)}{1 - h^2} \right\}, \tag{98}$$

the limit of which is M', however small b is taken. Similarly we should find

$$\lim_{\alpha \to b} \sigma dx = -\mathbf{M}', \tag{99}$$

\* The term 1/x arises as

$$\lim_{z\to 0}\int_0^\infty e^{-mz}\sin mxdm.$$

See the Appendix.

and so on. Now, referring to (91) we have

$$-\frac{dw_0}{dx} = \frac{M'g}{2\mu\alpha} \sum_{s} \left\{ 1 - \frac{\alpha^3}{\alpha^2 - \beta^2} \frac{1}{s\pi/\alpha + \alpha} - \frac{\beta^3}{\alpha^2 - \beta^2} \frac{1}{s\pi/\alpha - \beta} \right\} h^s \sin\frac{s\pi c}{\alpha},$$
(100)

where s = 1, 3, 5, ... Here

$$\sum_{s} h^{s} \sin \frac{s\pi x}{a} = \frac{h(1+h^{2}) \sin \frac{s\pi x}{a}}{1-2h^{2} \cos \frac{2\pi x}{a} + h^{4}},$$
 (101)

the limit of which is  $\frac{1}{2} \operatorname{cosec}(\pi x/a)$ . In the remaining terms we may put h = 1 at once. It is shown in the Appendix that for values of x between 0 and  $\frac{1}{2}a$ 

$$\sum_{s} \frac{\sin(s\pi x/a)}{s\pi/a + \alpha} = \frac{\alpha a}{2\pi} \int_{0}^{\infty} \frac{\cosh(\frac{1}{2}a - x)\eta}{(\eta^{2} + \alpha^{2})\cosh(\frac{1}{2}a\eta)} d\eta, \tag{102}$$

$$\sum_{s} \frac{\sin(s\pi x/a)}{s\pi/a - \beta} = \frac{1}{2} a \frac{\cos\beta(\frac{1}{2}a - x)}{\cos\frac{1}{2}\beta a} - \frac{\beta a}{2\pi} \int_{0}^{\infty} \frac{\cosh(\frac{1}{2}a - x)\eta}{(\eta^{2} + \beta^{2})\cosh\frac{1}{2}a\eta} d\eta. \quad (103)$$

It is not difficult to see that if  $\beta a$  be moderately large, but less than  $\pi$ , whilst  $\beta x$  is small, the result tends to the form

$$-\frac{dw_0}{dx} = \frac{\mathbf{M}'g}{4\pi\mu} \left[ \frac{1}{x} - \frac{\alpha^3}{\alpha^2 - \beta^2} \int_0^\infty \frac{\alpha e^{-\eta x}}{\eta^2 + \alpha^2} d\eta - \frac{\beta^3}{\alpha^2 - \beta^2} \left\{ \pi \cos \beta x - \int_0^\infty \frac{\beta e^{-\eta x} d\eta}{\eta^2 + \beta^2} \right\} \right],$$
(104)

which is equivalent to that above obtained.

If we impose periodicity there is in the present problem no indeterminateness, and no instability so long as  $\beta a < \pi$ . If we imagine a cylindrical earth, periodicity is essential in the solution, and there is no mathematical absurdity in regarding the points x = 0, x = 2a, for instance, as being the same place. The curvature would, of course, involve some modification of the elastic equations.

I have made some calculations illustrative of the formulæ (93), (94). To simplify the numerical work I have assumed  $\beta = \frac{1}{6}\alpha$ , which is not quite consistent with (90), but is equivalent to diminishing the value of  $\mu$  by about one-tenth. In Column I below the tilting effect  $(-dw_0/dx)$  is compared with that given by the formula (23) where gravity was altogether neglected. Column II gives the ratio of the *total* deflection

$$-\frac{d}{dx}(w_0+V_0/g)$$

to the value given by (23). It is remarkable that the numbers in Column II only differ by about 1 per cent. from those which we should obtain by

ax.	1.	II.	ax.	I.	11.
0.0	1.0	1 .3125	0.2	0 .5503	0 .760
0.05	0 .9265	1 .222	9.0	0.4912	0 .691
0.1	0.8641	1 ·145	0 .7	0 · 4457	0.686
0.2	0.7602	1 .017	0.8	0 .4050	0 .288
0.8	0.6757	0.914	6.0	0.3655	0.542
0.4	0.6048	0.827	1.0	0.3865	0.507

multiplying Column II of the Table on p. 301 by 1.3125, which is now the proper ratio required (instead of 1.348) to convert the tilting effects there considered into total deflections. This result might have been foreseen. Recurring to the typical formulæ (91) and (92) we note that

$$\frac{2\pi\gamma H}{g} = \frac{gH}{2\mu} \times \frac{4\pi\gamma\mu}{g^2} = \frac{gH}{2\mu} \cdot \frac{\alpha\beta}{(\alpha-\beta)^2}.$$
 (105)

Hence we find after a few reductions

$$-\frac{d}{dx}\left(w_0 + \frac{\mathbf{V}_0}{g}\right) = \frac{\alpha^2 - \alpha\beta + \beta^2}{(\alpha - \beta)^2} \frac{g\mathbf{H}}{2\mu} \left\{ 1 - \frac{\alpha^3}{\alpha^3 + \beta^3} \frac{\alpha}{m + \alpha} + \frac{\beta^3}{\alpha^3 + \beta^3} \frac{\beta}{m - \beta} \right\} \sin mx. \tag{106}$$

If  $\beta = \frac{1}{6}\alpha$  the last term in the bracket is small, and the expression is almost in a constant ratio to that which occurs in (50) provided  $\kappa$  be written for  $\alpha$ .

The deflections at given distances are, however, diminished from the values based on Art. 5 above, where undisturbed gravity was alone regarded in calculating the strains, and at great distances the effect is considerable. Since on the present reckoning,

$$\frac{\kappa}{\alpha} = \frac{\alpha - \beta}{\alpha} = \frac{4}{5},$$

any line in the above Table relates to a distance four-fifths as great as that implied in the corresponding line of the Table on p. 301. To take a numerical example, let  $\kappa x = 0.8$ , which means a distance of about 2300 km. The total deflection is then only 0.507 of that given by a purely elastic theory; on the basis of Art. 5 the ratio would be 0.579.

8. The investigation for the case of a load M concentrated at a point of the surface follows a parallel course. We should find

$$w_{0} = \frac{Mg}{4\pi\mu} \int_{0}^{\infty} \frac{m^{2} - \alpha\beta m/(\alpha - \beta)}{(m+\alpha)(m-\beta)} J_{0}(mr) dm$$

$$= \frac{Mg}{4\pi\mu} \left\{ \frac{1}{r} - \frac{\alpha^{3}}{\alpha^{2} - \beta^{2}} \int_{0}^{\infty} \frac{J_{0}(mr)}{m+\alpha} dm - \frac{\beta^{3}}{\alpha^{2} - \beta^{2}} \int_{0}^{\infty} \frac{J_{0}(mr)}{m-\beta} dm \right\}, \quad (107)$$

$$\frac{V_{0}}{g} = \frac{M\gamma}{g} \left\{ \frac{1}{r} - \frac{\alpha^{2}}{\alpha + \beta} \int_{0}^{\infty} \frac{J_{0}(mr)}{m+\alpha} dm + \frac{\beta^{2}}{\alpha + \beta} \int_{0}^{\infty} \frac{J_{0}(mr)}{m-\beta} dm \right\}. \quad (108)$$

The principal value of the indeterminate integral is, as shown in the Appendix,

$$P \int_{0}^{\infty} \frac{J_{0}(mr)}{m-\beta} dm = \pi K_{0}(\beta r) - \int_{0}^{\infty} \frac{J_{0}(mr)}{m+\beta} dm$$

$$= \frac{1}{2} \pi K_{0}(\beta r) - \left\{ \beta r - \frac{(\beta r)^{3}}{1^{2} \cdot 3^{2}} + \frac{(\beta r)^{5}}{1^{2} \cdot 3^{2} \cdot 5^{2}} - \dots \right\}. \quad (109)$$

From (107) we derive

$$-\frac{dw_0}{dr} = \frac{Mg}{4\pi\mu} \left\{ \frac{1}{r^2} - \frac{\alpha^3}{\alpha^2 - \beta^2} \int_0^\infty \frac{mJ_1(mr)}{m+\alpha} dm - \frac{\beta^3}{\alpha^2 - \beta^3} \int_0^\infty \frac{mJ_1(mr)}{m-\beta} dm \right\}, \quad (110)$$

with a corresponding formula for  $V_0$ . The former of these integrals is evaluated in (74). As regards the latter we have by differentiation of (109)

$$\frac{1}{\beta} P \int_0^\infty \frac{m J_1(mr)}{m-\beta} dm = \frac{1}{2} \pi K_1(\beta r) + \left\{ 1 - \frac{(\beta r)^2}{1^2 \cdot 3} + \frac{(\beta r)^4}{1^2 \cdot 3^2 \cdot 5} - \dots \right\}. \quad (111)$$

The following Table, calculated on the numerical assumptions adopted in the preceding section, gives in Column I the ratio which the surface depression  $w_0$  bears to the value given by the first term in (107). Column II gives the ratio of the tilting effect to that given by the first term of (110), whilst Column III gives the ratio of the total deflection to the same term. It is assumed that the use of the "principal values" of the indeterminate integrals can be justified by considerations similar to those adduced in the two-dimensional case.

ar.	1.	II.	III.	ar.	ı.	II.	III.
0.0	1.0	1.0	1 .8125	0.5	0 .8785	0 6884	0 -860
0.08	0.8839	0.9499	1 246	0.6	0 8265	0.5840	0.799
0.1	0.7852	0.9089	1 ·198	0.7	0 2871	0.5892	0.744
0.2	0.5992	0.8219	1 '092	0.8	0 .2542	0.4996	0.696
0.8	0 .5087	0.7508	1 '005	0.9	0 .2260	0 .4627	0.651
0.4	0.4812	0.6886	0.928	1.0	0 .2020	0 4297	0.610

The comments made at the end of the preceding section apply equally well to these results. Thus, if  $\kappa r = 0.8$ , the total deflection is 0.610 of the tilting effect given by a purely elastic theory, whereas on the assumptions of Art. 6 the ratio would be 0.690.

## APPENDIX.

The following are proofs of some of the formulæ employed in the paper. I do not expect that they are altogether new, but the literature of Bessel's functions (for instance) is so diffuse, and the proofs so entangled, that it is

sometimes difficult to find a concise demonstration, even of an important formula.

## (A) The equation

$$f''(x) + \frac{1}{x}f'(x) + f(x) = \frac{1}{x}$$
 (112)

is satisfied by

$$f(x) = \int_0^\infty \frac{J_0(z)}{z+x} dz,$$
 (113)

and also by

$$f(x) = \int_0^\infty e^{-x \sinh u} \, du,\tag{114}$$

x being of course assumed to be positive. For (113) makes

$$f''(x) + \frac{1}{x}f'(x) + f(x) = \int_0^\infty \left\{ \frac{2}{(z+x)^3} - \frac{1}{x(z+x)^2} + \frac{1}{z+x} \right\} J_0(z) dz$$

$$= \int_0^\infty \left\{ J_0''(z) - \frac{1}{x} J_0'(z) + J_0(z) \right\} \frac{dz}{z+x}$$

$$= -\frac{1}{x} \int_0^\infty J_0'(z) dz = \frac{1}{x}, \qquad (115)$$

by partial integrations, and in virtue of Bessel's equation. Again (114) makes

$$f''(x) + \frac{1}{x}f'(x) + f(x) = \int_0^\infty e^{-x\sinh u} \left(\cosh^2 u - \frac{1}{x}\sinh u\right) du$$
$$= -\frac{1}{x} \int_0^\infty d\left(e^{-x\sinh u}\cosh u\right) = \frac{1}{x}. \tag{116}$$

The difference between the integrals in (113) and (114) must therefore be of the form

$$AJ_0(x) + BK_0(x)$$

where  $K_0$  is defined by (73) ante. Now the leading terms in the asymptotic expansions of  $J_0(x)$  and  $K_0(x)$  for large values of x are

$$\left(\frac{2}{\pi x}\right)^{\frac{1}{2}}\sin\left(x+\frac{1}{4}\pi\right)$$
 and  $\left(\frac{2}{\pi x}\right)^{\frac{1}{2}}\cos\left(x+\frac{1}{4}\pi\right)$ ,

respectively, whereas either definite integral is evidently at most of the order 1/x. It follows that A = 0, B = 0, and therefore

$$\int_0^\infty \frac{J_0(z)}{z+x} dz = \int_0^\infty e^{-x \sinh u} du, \qquad (117)$$

as stated in (71).

\* 'Hydrodynamics,' Art. 194.

(B) Consider the integral

$$\int \frac{e^{i\zeta x}}{\zeta + \beta} d\zeta, \tag{118}$$

where  $\zeta = \xi + i\eta$ . Let this be taken round the contour of the infinite region lying above the axis of  $\xi$ , the point  $\zeta = -\beta$  being excluded by a small semicircle described about it. The infinitely distant parts of the contour contribute nothing to the final result, and we find

$$P\int_{-\infty}^{0} \frac{e^{i\xi x}}{\xi + \beta} d\xi - \pi i e^{-i\beta x} + \int_{0}^{\infty} \frac{e^{i\xi x}}{\xi + \beta} d\xi = 0, \qquad (119)$$

or

$$P \int_0^\infty \frac{e^{-i\xi x}}{\xi - \beta} d\xi = \int_0^\infty \frac{e^{i^2 x}}{\xi + \beta} d\xi - \pi i e^{-i\beta x}.$$
 (120)

Hence, separating the real and imaginary parts,

$$P \int_0^\infty \frac{\cos \xi x}{\xi - \beta} d\xi = -\pi \sin \beta x + \int_0^\infty \frac{\cos \xi x}{\xi + \beta} d\xi, \tag{121}$$

$$P \int_0^\infty \frac{\sin \xi x}{\xi - \beta} d\xi = \pi \cos \beta x - \int_0^\infty \frac{\sin \xi x}{\xi + \beta} d\xi.$$
 (122)

The latter formula has been assumed in (109).

(C) If in (121) we write  $r \cos \theta$  for x, and integrate with respect to  $\theta$  between the limits 0 and  $\frac{1}{2}\pi$ , we obtain

$$P\int_{0}^{\infty} \frac{J_{0}(\xi r)}{\xi - \beta} d\xi = -2 \int_{0}^{\frac{1}{4}\pi} \sin(\beta r \cos\theta) d\theta + \int_{0}^{\infty} \frac{J_{0}(\xi r)}{\xi + \beta} d\xi, \qquad (123)$$

since

$$J_{\theta}(\xi r) = \frac{2}{\pi} \int_{0}^{\frac{1}{2\pi}} \cos(\xi r \cos \theta) d\theta. \tag{124}$$

Again, writing  $r \cosh u$  for x, in (122), and integrating from u = 0 to  $u = \infty$ , we have

$$P \int_0^\infty \frac{J_0(\xi r)}{\xi - \beta} d\xi = \pi K_0(\beta r) - \int_0^\infty \frac{J_0(\xi r)}{\xi + \beta} d\xi, \qquad (125)$$

in virtue of (73), and of Mehler's formula

$$J_0(\xi r) = \frac{2}{\pi} \int_0^\infty \sin(\xi r \cosh u) du. \tag{126}$$

By combining the formulæ (123) and (125), we obtain another proof of (74).

(D) To sum the series in (102) we take the integral

$$\int \frac{\cos(\frac{1}{2}a - x)\zeta}{(\zeta + a)\cos(\frac{1}{2}a\zeta)}d\zeta \tag{127}$$

round the contour of the infinite region lying to the right of the axis of  $\eta$ ,

the poles of the integrand being excluded as usual by small circles drawn round them. These poles are at the points

$$\zeta = s\pi/a, \quad [s = 1, 3, 5, ...],$$
 (128)

and the value of the integral taken in the negative direction round any one of them is

$$\frac{4\pi i}{a} \frac{\sin(s\pi x/a)}{s\pi/a + \alpha}.$$
 (129)

If x be positive, and  $<\frac{1}{2}a$ , as we will suppose, the part of the integral due to the infinitely distant portions of the boundary will vanish. The sum of the series of terms of the type (129) is therefore equal to

$$\int_{-\infty}^{\infty} \frac{\cosh\left(\frac{1}{2}\alpha - x\right)\eta}{(i\eta + \alpha)\cosh\frac{1}{2}\alpha\eta} id\eta. \tag{130}$$

This leads to the formula (102).

In the case of the integral

$$\int \frac{\cos(\frac{1}{2}\alpha - x)\zeta}{(\zeta - \beta)\cos\frac{1}{2}\alpha\zeta}d\zeta,\tag{131}$$

there is an additional pole  $\zeta = \beta$ , which gives a term

$$-2\pi i \frac{\cos\beta\left(\frac{1}{2}a-x\right)}{\cos\frac{1}{2}\beta a}.$$
 (132)

The formula (103) easily follows.

# Torsional Hysteresis of Mild Steel.

By J. J. GUEST and F. C. LEA.

(Communicated by Sir Oliver Lodge, F.R.S. Received November 2, 1916.)

The stress-strain curve from no load to fracture for mild steel as usually obtained consists of three parts: (1) A straight line, followed by a part deviating only slightly from this straight portion; (2) a sharp bend, followed by a part approximately parallel to the strain axis; and (3) a curved rising part, leading ultimately to the breaking point. It is generally assumed that Hooke's Law holds throughout the part (1), and is immediately followed by the sharply defined bend which constitutes the yield point. For mild steel first stressed in tension and then in compression, or subjected to positive and then negative torsional stresses, the stress-strain curve within a considerable range of stress is also supposed to be a straight line.

It is further well known that if mild steel is stressed in tension beyond the yield point the elastic limit is raised, but only at the expense of lowering it in compression; or, if it is twisted beyond the yield point in one direction, its elastic limit is raised for stresses in that direction, but lowered for those in the opposite direction. Attempts have been made to relate the range of stress through which the stress-strain curve is a straight line with that through which a material, such as mild steel, can be stressed an infinite number of times without fracture. This is expressed by the well known Bauschinger's Law, which, as stated by Mr. Leonard Bairstow,\* is as follows:--" The superior limit of elasticity can be raised or lowered by cyclical variations of stress, and at the inferior limit of elasticity will be raised or lowered by a definite, but not necessarily the same, amount. The range of stress between the two elastic limits has therefore a value which depends only on the material and the stress at the inferior limit of elasticity. This elastic range of stress is the same in magnitude as the maximum range of stress, which can be repeatedly applied to a bar without causing fracture, no matter how great the number of repetitions."

In the paper by Mr. Leonard Bairstow, just referred to, its author, in discussing the stress-strain curve obtained after a certain number of repetitions through a given range of stress from a mild steel specimen, remarks:—
"The behaviour of this specimen illustrates the necessity for Bauschinger's hypothesis relating to primitive elastic limits, as the extensometer was

<sup>\* &</sup>quot;Iron and Steel under Cyclical Variations of Stress," 'Phil Trans.,' A, vol. 210 (1909).

incapable of showing the first deviations from elasticity. At a slightly lower range, probably 13 tons per square inch, the specimen would have been really elastic, as no number of reversals would have produced a hysteresis loop." On the other hand, others have suggested the existence of a hysteresis loop when mild steel is stressed through ranges within the "primitive elastic limits." Prof. Ewing and others, from experiments on wires, have supposed its existence.

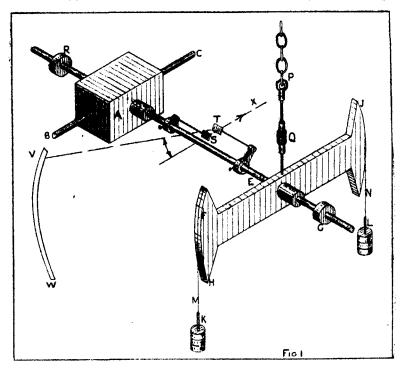
It is doubtful, however, whether the results of experiments on wires can be taken as holding for material in a more normal state. Experiments by Lea on hard drawn steel tubes certainly show that the material of such tubes is in a very different condition to hot worked or annealed steel. Experiments by Guest, an example of which is given in the 'Phil. Mag.,' July, 1900, p. 89, showed definite hysteresis loops in Swedish iron under tension, but this does not appear to have been confirmed by other workers—probably from lack of instruments having the necessary precision—and whether or not such a hysteresis loop does exist and the effect upon it of various treatments of the material, although probably a matter of very considerable practical importance, as also of scientific interest, as likely to throw light upon doubtful matters, does not appear to have been subjected to adequate investigation.

The general failure to establish clearly the existence of a hysteresis loop for mild steel stressed alternately in tension and compression, and the difficulty of reversing stresses readily from tension to compression, suggested the desirability of making an accurate and sensitive torsion machine, in which a specimen could be subjected to pure torsion in either a clockwise or anti-clockwise direction, and in connection with which angular strains could be measured with very great precision. Designs for such a machine were accordingly prepared by Mr. Guest in 1912, and the machine was constructed by Prof. Lea in the Civil Engineering Department of the University of Birmingham, and was erected, after military occupation of the University Buildings in 1914, by the kind permission of Sir Oliver Lodge in his laboratory at Edmund Street.

### Description of the Apparatus.

The machine itself consists of a head A, Fig. I, carried on an axis BC, supported horizontally by a bracket, and holding the specimen DE so that it is perpendicular to BC. The other end E of the specimen is secured to a rocking arm FJ, having turned arcs FH and JN. This arm is supported immediately by the equivalent of a universal joint, containing a ball bearing within the arm; this is not shown in the diagram. The axis of the

specimen is set to be horizontal by means of the right and left turnbuckle Q in the tackle supporting the rocking arm. The anchorage of the suspension



chain P has an adjustment parallel to the axis of the specimen, so that various lengths of specimens can be accommodated and the chain set vertical. From the area FH and JN the weight-carriers K and L are suspended by the steel strips M and N; these are loaded by hand, weights on one side giving positive and on the other negative torques.

A rod, with an adjustable weight R, projects from the rear of the head A. so that the head, together with any fraction of the specimen determined upon, can be balanced, and thus zero bending moment at any desired crosssection of the specimen can be secured. Similarly, the balance of the rocking arm about a horizontal axis perpendicular to the specimen can be adjusted by the weight G, so that zero bending moment can be enforced at a second cross-section of the specimen. The rocking arm was weighted so that its centre of gravity was just below the axis of the specimen, making the equilibrium just stable.

The arrangement, see Fig. I, for measuring the twist consists of a mirror S carried on a rod held in a frame attached to the specimen near its fixed end D, and a second mirror T similarly carried near the other end E of the VOL. XCIII .-- A. 2 B

specimen. These are set opposite to each other with their reflecting faces parallel to the axis of the specimen. The twist between the points of attachment of the mirror frames is read at a single reading of the scale VW, Fig. I, by a telescope at X, the course of the light being indicated by the broken line. The scale is bent into an arc, with T as centre, to avoid the necessity for correction and to preserve the sharpness of definition of the telescope.

The machine is designed on such a scale that hollow specimens machined from the solid can be employed, and the use of drawn metal avoided. A solid specimen,  $\frac{7}{8}(0.8755\pm0.00025)$  inch diameter and 16 inches long between the points of attachment of the mirror frames, has been used in this research.\*

Tests for sensitiveness of the rocker arm showed that it turned freely when not attached to the specimen, with an addition of 0.05 lb. on one weight-carrier, when each carrier was loaded with 100 lb. The sensitiveness of the apparatus, with the specimen in position, was also tested at various loads during the course of the experiments.

With the above-mentioned specimen in position, small load variations showed that the machine was readily sensitive to loads corresponding to the degree of accuracy with which the scale could be read—0.002 inch.

The weights used were all adjusted to 0.1 oz., and, when necessary, care was taken to employ them in the same order, thus any small inaccuracies in the determination of this mass have no appreciable effect upon the hysteresis loops presently to be described.

The diameter of the rocker was 40 inches, so that a load of 1 lb. produced a torque of 20 inch-lb., corresponding to a maximum stress in the bar of 152 lb. per square inch.

The scale used was 25 inches long, divided into fiftieths of an inch, and was set up at a distance of 94 inches from the mirror T. The magnification of the telescope was such that the fiftieth divisions could readily be subdivided into tenths by estimation. Thus, a scale reading of 1 inch corresponds to a shear strain of  $0.8755 \div (4 \times 16 \times 94) = 0.0001454$  radians, and the readings were made to  $\frac{1}{100}$  of this, or 0.000000291 radians.

During the experiments the bar was loaded beyond the yield point, and in order to follow the strain over the range involved in the permanent set obtained, the zero on the scale was shifted. To do this the mirror-holder at the outer end of the bar was unclamped, and simply rotated in its carrier

<sup>\*</sup> The analysis of the steel used in the experiments, kindly supplied by Messrs. Vickers, gave the following percentages:—Carbon 0.15, manganese 0.30, phosphorus 0.037, sulphur 0.033, silicon 0.055.

frame about an axis parallel to the specimen, and reclamped; the apparatus was designed to permit of this being easily done.

Before inserting the specimen, the head and rocker were balanced so that there should be zero bending moment at two surfaces in the specimen at about a quarter the distance of the point of attachment of one mirror frame from the other. The chain anchorage was then adjusted so that the chain was vertical with the specimen in position. The specimen was inserted, and levelled by the use of the right- and left-hand screw buckle. The weight-carriers were then loaded equally and sufficiently to give steadiness while passing through zero loads. Finally, the mirror frames and telescope were set in position.

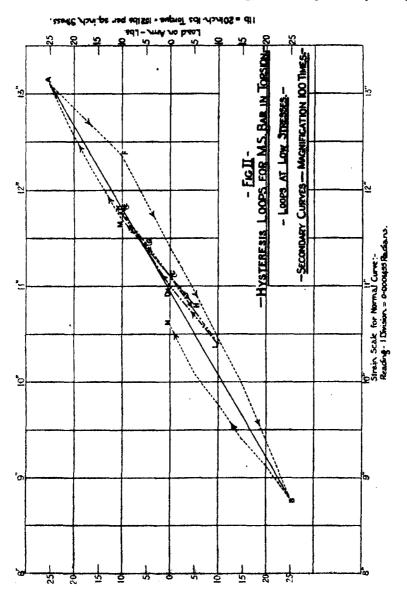
From a considerable number of tests, typical examples have been selected 'illustrative of the various points investigated in the course of the experiments: (1) the existence of hysteresis loops at low loads (Fig. II); (2) their relation to those over a wider (but elastic) range and to small loops at high average stress (Fig. III); (3) the effect of plastic overstrains (Figs. IV and V), of rest (Fig. VI), and of mild heat treatment (Figs. VII and VIII).

In Table I and Fig. II are shown the results of some tests on the bar with low loads. The stress curve AB, which in the sequence is referred to as the natural stress-strain curve, is plotted to the scales shown on the figure. It appears to be a straight line, the differences of the strains obtained by rising and falling loads not being visible on the scale to which AB is drawn. To render these differences perceptible, a geometrical straight line joining the points A and B is considered, and the differences of the observed strains, from those corresponding to the geometrical line AB, are multiplied 100 times, and set off either to the right or left of this line, according as the observed strain is greater or less than that corresponding to the geometrical line. Thus, suppose the diagram to start from the point C. On the normal scale the point C is on the line AB, coinciding with the point D. On loading with +5 lb., taking off the load and loading with -5 lb., taking off and reloading with +5 lb., the diagram on the exaggerated scale is HG, with no width to the hysteresis loop. On the natural scale, the part corresponding to HG is indistinguishable from the portion of the line AB, obtained by projecting HG horizontally on to it. On now loading to -10 lb., and then unloading by intervals of 5 lb. to zero, and loading to +10 lb. and back to zero, the small loop CLDKC on the secondary scale is obtained. Actually, in this experiment this loop CLDKC was taken before HCG (see Table I). By loading to 25 lb., unloading to zero, loading to -25 lb., and unloading to zero, the much larger loop CMAFBN is obtained. All the parts of these loops, when

Table I (from which Fig. II has been plotted).—Scale Readings in Inches. The arrows indicate the sequence in loading. 8 -788 ä 9 ·223 9 ·218 ଞ୍ଚ 9 ·658 9 ·646 2 Negative. 10 -090 10 -076 10-087 10. 10 ·523 10.520 က် 10.778 Net torque load in lbs. 10 **·954** 10 938 10 -948 10 -947 Ö સં 11 376 11 376 11 386 ïĊ 11.806 11 ·805 11 ·818 11.806 10. Positive. 12 :236 12 :246 15. 12 ·668 12 ·674 8 13.102 S.

plotted on the natural scale, appear to be within the width of the physical straight line AB.

In the secondary curves all observation points are joined by straight



lines, no attempt having been made to ease off any errors by drawing smooth curves. This description will make clear the procedure in connection with the succeeding curves. In all cases a geometrical line similar to AB is

taken as an axis of stress, from which the secondary curve strains are plotted. The slope of the line AB gives the modulus of rigidity "C" for the range of loading of  $\pm 25$  lb., or range of stress  $\pm 3800$  lb. per square inch, and, if plotted only on the natural scale, it would appear to be constant. The exaggerated secondary curves show, however, that it varies slightly with the range of loading. The value of the modulus for the bar is about 5390 tons per square inch.

In Fig. III is shown in a striking manner the increase in the size of the hysteresis loop for larger ranges of stress, and also the small hysteresis loops obtained by increasing and decreasing the load at any stage in the circuit. Again, the secondary curves are plotted from the line AB, but they are exaggerated 50 instead of 100 times.

The sequence of the tests is shown by arrowheads on the diagram and by the figures in Table II. Starting at the point C on the zero stress line, a 50-lb. cycle was taken, and is shown marked No. 1; a 50-lb. half-cycle, marked No. 2, is then drawn. It terminates at D, and is followed by eycles 3 (through E and terminating at F), 4 (to G), 5 (to M), and a half-cycle 6 (to L) taken to loads of ±100 lb., with a number of small loops (such as GNHG), having a range of 20 lb., taken at various stages of the loading. For clearness of the figures, the loops 5 and 6 have been shifted vertically, the line A'B' being the new position of the line AB. Different types of broken lines are used to aid lucidity. The course of the observations is indicated by the arrowheads on the secondary curves and by the arrows in Table II. The width of the hysteresis loops increased with the range of loading. It will be noticed, however, that, wherever on the range of stress the small included loops were taken, the widths for a definite range were nearly constant, but were rather greater near the zero load line than at the loaded parts of the main curve. The value of C, which has previously been decreasing, shows a very slight rise in the ±100-lb. cycles. The central pair of small loops are inclined to the main curve at the point where they branch from it, and, compared with AB, they give a slightly higher value for the rigidity. The unloading side of the other pair of small loops coincides with the unloading line of the main hysteresis loop.

In these tests there was no perceptible permanent creeping at any definite point, but a small amount apparently occurred towards the -100 lb. loading, as shown by the curve 4 not coinciding exactly with 3. Except for this, within all these hysteresis loops the strain arrived at was definite and unaffected by time. The strain, however, at any or no load, depends upon the previous history. Thus at no load the specimen has been successively left with the strains indicated by the points CDEFGHKLM, and the

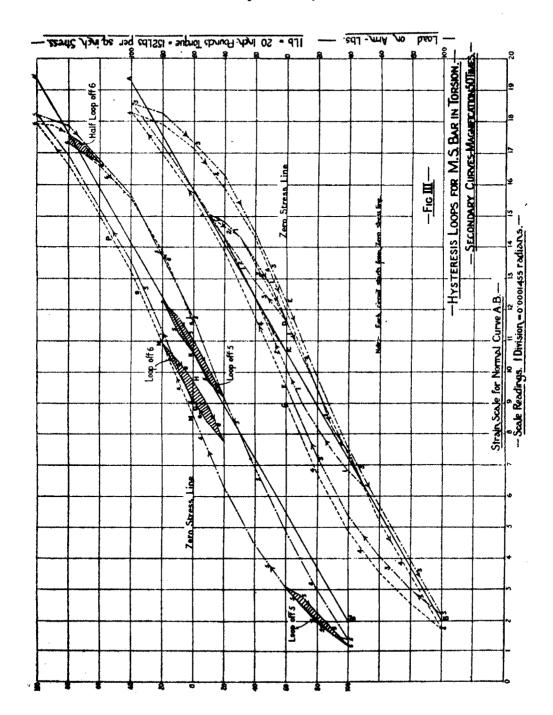


Table II (from which the loops 1 to 6, Fig. III, have been plotted).—Scale Readings in Inches. The arrows indicate the sequence of loading.

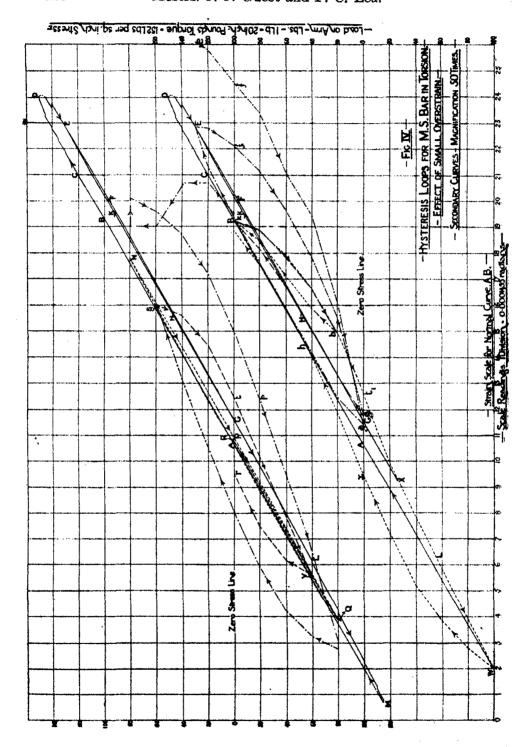
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material may be left at the stress and strain represented by any point within the main hysteresis loop without the manifestation of any time effect. The width of this part LM on the natural scale would show as one-twentieth of one scale division. The material may, from this point of view, be said to have slight permanent set, although there is no evidence of a time effect. The narrower the hysteresis loop over the range of stress considered, the more perfectly elastic the material may said to be.

The initial behaviour of the specimen upon any test then depends upon the previous history. Thus, for example, if the specimen be left in the state represented by the point M, the initial line will be along MNP; but left in the state G, the initial line will be along GNP.

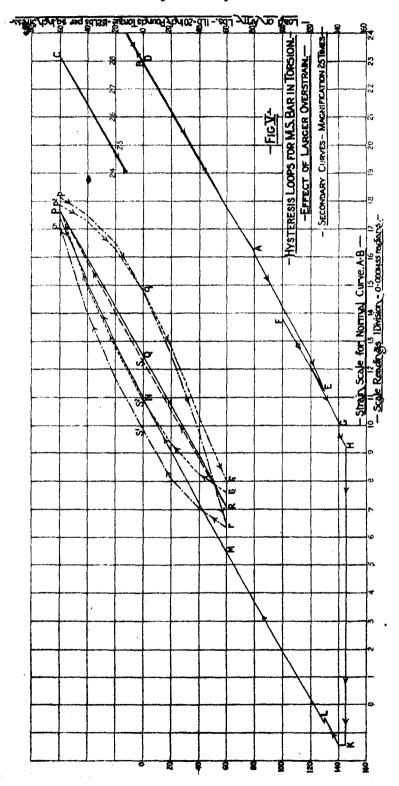
The effect of a slight overstrain of the material is shown in Fig. IV, which is again divided into two parts, and has the secondary figures exaggerated fifty times. Before the material was overstrained, the loops GBbBbXWh were taken. The whole actual stress-strain curve (ABCDEFGHKEFGLMANPQR) is shown completely in the upper figure and contains loops of such magnitude as to be visible upon the normal scale. In this test the amount of permanent overstrain AG involved at zero stress is small compared with the strain which the material can sustain without time effects. loading, "creep"—that is, slow increase of strain with time without alteration of load—first occurred at C, 120 lb. load (see Table III), and the main extension at I) (150 lb.), while the strain continued to increase when the load was reduced to 140 lb. The loop EFGHKE shows no creep, but on continuing the curve to negative stress very distinct creep appears at L (upper figure) 60 lb. only. An exaggerated curve  $efghkEf_{1}q_{1}$  (lower figure) is drawn. This is not closed as the loops in Fig. II were; also  $\mathbb{E}f_1g_1$  lies within efg, or the second unloading curve lies within the first. Secondary curves for later observations are also drawn. These show that after overstraining the material to the slight amount shown on the main curve, the internal condition of the material is upset, and, at any rate for some time, no actual straight line exists. At the load -60 lb. (point L) very slight creep occurs and the width rt (upper part of figure) of the hysteresis loop SV for +60 lb. is nearly as wide as the width xt (lower part of figure) of the loop BW for the  $\pm 100$  lb. cycle taken before the overstrain.

Similar curves for overstrain are given in Fig. V, where a much larger amount of overstrain (here negative) is employed. The natural curve starts from A (-80 lb.) and passes through B to C (60 lb.), returning through D to A, and then through E back to F, and again on through G to H (-145 lb.) where the large overstrain (HK) occurs. On the return, creep continued on the load being reduced to L (-130 lb.), and the following stress-strain



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• This oresp took place in 2 minutes.



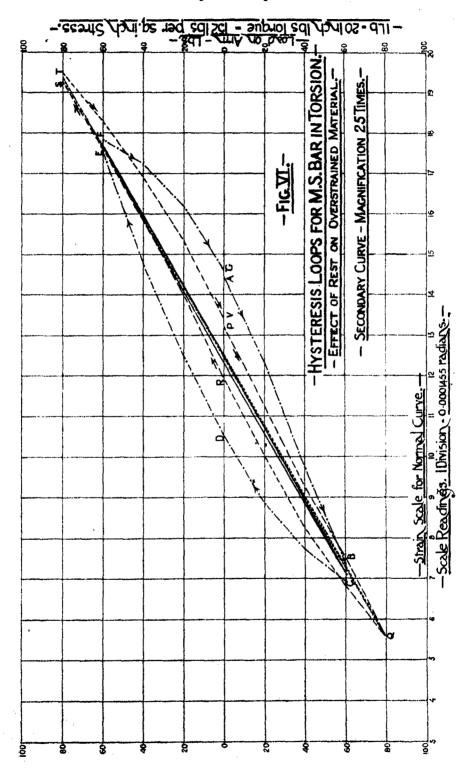
line is decidedly curved. Restoring creep began to occur at M (-60 lb.), and is well marked at no load N, and at the succeeding positive loads. After P (+60 lb.) the load was reduced, a loop PQRSP being formed. This and the succeeding loop are given in the secondary curve (exaggerated 25 times)  $pqrs_1 p_1 p_2 qr_1 r_2 s_2 p_3$ . Thus after an overstrain HK a little less than the preparatory elastic strain, the stability of the material is upset, creep occurring at  $\pm 60$  lb. load, and the width of the loop is very considerable. In comparing the secondary loops of Fig. V with those of Figs. III and IV it must be borne in mind that the magnification is only 25 as against 50 times.

## Effect of Rest on Overstrained Material.

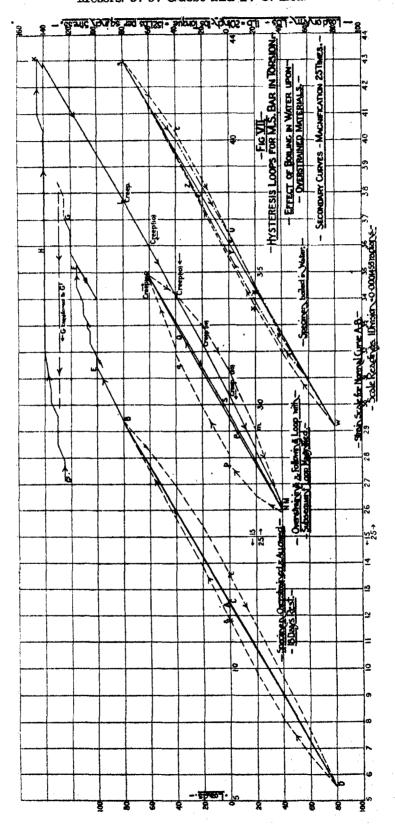
The effect of rest upon the material is shown in Fig. VI, in which again the secondary curves are exaggerated 25 times. Shortly after the overstrain of Fig. V the loop, of which the secondary curve is ABCDEFG, Fig. VI, was taken, and this shows creep BC and EF at  $\pm$  60 lb. loading. After 10 days' rest the specimen was re-tested and the secondary loop PQRSTV obtained; no creep occurred at - 80 lb. but a small amount ST occurred at + 80 lb. (so that V does not join up to P). The width of the loop is reduced by this rest to less than half its previous amount. The loops are sufficiently wide to be shown on the natural stress-strain curves. The range of stress without creep is also considerably increased by this rest. The natural curve taken soon after the overstrain is shown in the full lines and that after rest in dotted lines, while the secondary curves are drawn by alternate dot and dash, and by dashes respectively.

#### Effect of Heating Overstrained Material,

The effect of boiling (at 100 °C.) upon the material is shown in Fig. VII, in which the exaggeration is again 25 times; 18 days after the previous overstraining, a test running between  $\pm$  80 lb. gave the natural loop ABCI), with no creep, which is shown exaggerated at aBcD and is to be compared with the loop of Fig. VI taken after a shorter rest, 10 days. The test was continued—showing creep first at E (100 lb.)—in order to give the overstrain indicated by EFGG'HK (mainly at 140 lb.) when the load was reduced and a loop obtained as indicated by the line KLMNPQRSN. To keep this figure within bounds G has been transferred to G', whence the curve continues along G'H'K. In the loop NPQRSN creep occurs. During reduction of load from + 145 lb. creep occurred at L (+ 80 lb.) and continuously afterwards, at 60 lb., at 40 lb. and lower loadings. It also persists in the following loops, as is clearly shown in the secondary figure NpqRmN. The specimen was then boiled in water for one hour and afterwards the loops (shown in the figure on



Messrs. J. J. Guest and F. C. Lea.



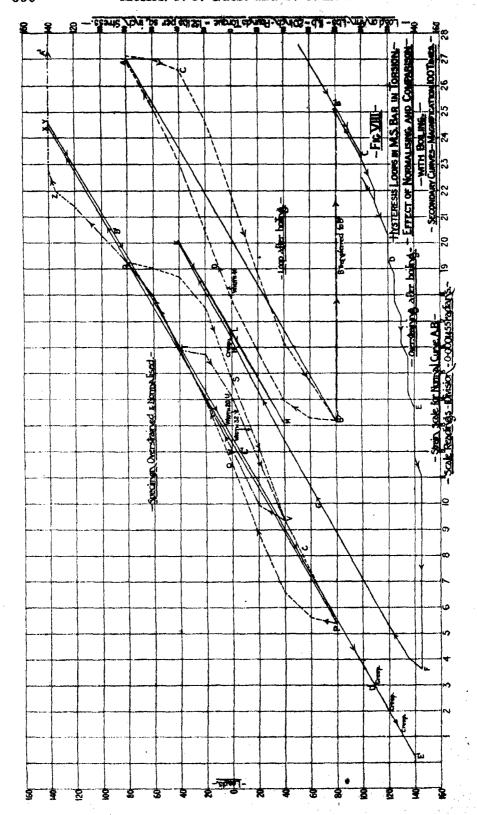
the right) between 60 and 80 lb. were taken for comparison with the loops aBcDa and NpqRmN respectively. The loops obtained after boiling are very much narrower than those shown on the left of the figure, the width on the natural curve being covered by the width of the tapering line WS. Compared with the loop taken after 18 days' rest, the width of the loop WazStUW is about two-thirds that of aBcDa. The same loop is shown at BDAC in Fig. VIII but the magnification here is 100. After taking the loop BDACB, Fig. VIII, the curve is continued along B'CDEF, showing creep at C and a considerable permanent set at EF. The unloading curve is FGH and is followed by the loop HKLMK clearly seen on the natural curve. As before, return creep took place on the unloading curve, the condition of the material having been upset.

The specimen was then tempered, or as it is sometimes termed normalised, by being maintained at  $330^{\circ}$  C. for one hour in an electrically heated furnace. It was then re-tested. In the natural curve obtained after heating all the observations are included in the width of the thickness of the taper line PX. The secondary curves PQRSVP of the loop for  $\pm$  80 lb. loading is drawn for comparison with the loop ABCD, Fig. VIII, obtained after boiling, its width being about three-quarters of the latter. A second exaggerated loop TUVWT between  $\pm$  40 lb. was then taken and the loading was afterwards continued as shown on the natural curve RX up to 140 lb. load, when a sudden yield XY occurred without signs of previous creep. The secondary figure for this loading is shown at WTRZXA'. A very small overstrain was permitted and the load gradually reversed, giving the line YB'C'D'E'. Creep occurred at D' (-110 lb.) and a yield at E' -140 lb. loading.

In all the above cases considerable yield occurred at about 140 lb. (+ or -) and sometimes yielding continued after the load had been reduced, but after heating at 330° C. no creep took place before the yield at 140 lb. After overstraining followed by rest or boiling at 100° C. creep occurred at less than 140 lb., so that normalising at the above temperature considerably extended the range in which the hysteresis loop is narrow and in which the material shows no sign of creep.

It has not been thought necessary to include Tables from which all curves have been plotted, as the three given are quite representative of the results obtained during the tests.

The particulars given in this paper are but a commencement of the researches it is proposed to carry out, but they clearly demonstrate the existence of a hysteresis loop at stresses considerably below the generally accepted elastic limits for mild steel, and they further show the beneficial effect of rest and of mild heat treatment.



One of the authors\* has shown that the elastic limit in compression, as measured by an ordinary extensometer, of cold drawn steel tubes is very considerably raised by tempering at temperatures from 300° to 550° C.

During the severe treatment to which mild steel is subjected in cutting machinery the material is locally stressed so as to leave conditions of overstrain. After overstrain the material gradually, with time, acquires a more "normal" state, but a more perfect state is rapidly produced by slight heat treatment as above described. In several establishments manufacturing precision machinery the parts are allowed a considerable period of rest before the final operations are performed upon them, but one of the authors has used such heat treatment (temperature of boiling water and oils) for the past 15 years in the production of accurate machine details.

Another point that the experiments indicate is that the yield of a bar under torsion may be much more sudden than it is generally thought to be. After tempering the specimen at 330° C, the tendency to creep at less torsion loads than 140 lb. was nearly eliminated (entirely in the example of Fig. VIII), but at 140 lb. a remarkably sudden yield occurred. The observation of this was very striking. The load was applied to the arm by small instalments and slowly. Upon reaching what proved to be the yield point load, for a short time no sign of yield occurred; the specimen then began to give way slowly and soon the rate of yielding became rapid and the bar twisted through a considerable range. The abruptness of yield appears, as is to be expected, to depend upon the uniformity of the material.

As the stress in a shaft under torsion reaches a maximum at the outer surface, the suddenness of this yield (after normalising) indicates that when the stress is close to the yield point the material is really unstable. The yielding of the outside thus starts the yield of the adjacent material which is not so highly stressed and which thus apparently yields at a lower stress than that at which the outside material yielded. If this were not so the yield of the outer material could only produce a small twist in the specimen as a whole.

Since fatigue effects depend upon the gradual increase of the width of the hysteresis loop with repetition, it would appear that boiling and tempering at comparatively low temperatures remove initial strains, and thus considerably increase the resistance of the steel to repetition stress. Hence parts to be subjected to such stresses, and materials, such as tubes, subjected to cold drawing can, with advantage, be normalised. One of the authors† has for some years advocated the adoption of this treatment for such articles as crank shafts.

<sup>\* &#</sup>x27;Recent Researches on Tubular Steel Struts,'

<sup>† &#</sup>x27;Proc. Inst. Automobile Engineers,' vol. 6 p. 365.

One more point is worthy of note, After overstrain it has been stated that negative creep occurred at diminishing loads, or, in other words, as the loads were decreased the twist of the bar diminished while the load was steady at a given amount. This is accounted for, if it be assumed that the stress near the surface of the bar is beyond the elastic limit, while nearer to the centre it is still within the elastic limit. Hollow specimens of various kinds of steel are to be tested as soon as opportunity offers.

The results obtained in these preliminary experiments are not such as to allow of definite conclusions being drawn as to the behaviour of material in general, but there seems to be no doubt that, for the mild steel used in these tests, the torsion stress-strain curve for a rising or falling load does not obey Hooke's Law, and that for a given range of torsion, well below that which produces a stress equal to what is generally considered the elastic limit of a mild steel, whether wholly positive, negative, or changing sign, a hysteresis loop is obtained and the elastic limit as at present defined would appear to be zero.

An examination of the curves given in the paper shows that for any given value of the torque, the slope of the stress-strain curve, and thus the modulus of rigidity, depends upon the way the stress is changing, and at any given stress, including zero stress, is not a constant quantity, but depends upon the previous history of the material.

The thanks of the authors are due to Mr. M. Parkes, Stud. Mem. Inst. C.E., for his skilled assistance in preparing the drawings from which the curves have been reproduced.

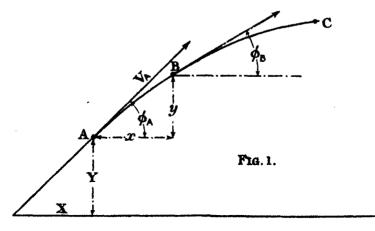
## A Graphical Method of Drawing Trajectories for High-Angle Fire.

By W. E. DALBY, F.R.S.

(Received January 25, 1917.)

In May, 1915,\* I described a graphical method for finding the time of flight, the range, the angle of elevation, in fact, the elements of a trajectory, having given the curve of resistance as a function of the velocity and assuming that the density of the air was constant at all points along the trajectory. The method is therefore only applicable to trajectories of low altitude. In this paper I describe a graphical method for obtaining a series of points on a trajectory of high altitude, taking into account the variation of the density of the air with height.

Let A, fig. 1, be a point on a trajectory where the velocity is given and equal in direction to  $\phi_{\mathbf{A}}$  and in magnitude to  $\mathbf{V}_{\mathbf{A}}$ , and whose position is given by the co-ordinates X and Y. The problem is to find the co-ordinates x, y,



with reference to the point A, of a second point B, on the trajectory, taking into consideration the actual resistance of the air to the motion of the shell, it being assumed that the variation of the density of the air is known as the shell rises or falls in height; and to find the angle  $\phi_B$  defining the direction of motion and the magnitude of the velocity at the point B in the trajectory.

Providing that two curves are given, the problem may be solved approximately by a process of step-by-step integration, using the graphical method

<sup>\* &#</sup>x27;Roy. Soc. Proc.,' A, vol. 92, p. 829 (1916).

explained in my paper\* to obtain time-velocity and time-distance curves.

These two curves are:—

- (1) A curve showing p, the resistance in air of standard density of a shell of standard form fired under standard conditions, the resistance being shown as a function of the velocity (such a curve is shown in fig. 3).
- (2) A curve showing the tenuity  $\tau$  of the air as a function of the height (as shown in fig. 7, p. 344). The tenuity  $\tau$  at height h is the ratio between the density of the air at height h and the standard density at sea-level.

According to the official text-books the resistance to motion through the air is then proportional to  $\tau p$ , and for a shell of diameter d the resistance is equal to  $k\sigma d^2\tau p$ , where k is a coefficient to allow for the shape of the shell and  $\sigma$  is a coefficient to allow for the steadiness, a technical term used to include such variations as may be produced by irregularities in the actual firing. The resistance expressed in this way is also in accord with the method given in the official gunnery text-book.

### Solution of Problem.

The given velocity at the point A in the trajectory (fig. 1) has components

 $V_A \sin \phi_A$  vertically,

V<sub>A</sub> cos φ<sub>A</sub> horizontally.

The resistance in the trajectory corresponding to the velocity  $V_A$  is found from the curve fig. 3 to be  $p_A$ . The corresponding component resistances at A are:—

 $p_{A} \sin \phi_{A}$  vertically,

 $p_{\rm A}\cos\phi_{\rm A}$  horizontally.

Then, putting E for the constant  $k\sigma d^3$ , the resistances against which the shell rises vertically are the air resistance  $E\tau p\sin\phi$ , and the weight of the shell w, giving a total resistance of  $(E\tau p\sin\phi + w)$ . When the shell is rising the two terms are of the same sign, but when falling they are of opposite sign.

The resistance against which the shell moves horizontally is  $E\tau p\cos\phi$ . The equations of motion are:—

$$-(\text{E}\tau p\sin\phi + w) = \frac{w}{g}\frac{dv}{dt} \text{ vertically,} \tag{1}$$

$$-(\mathbf{E}\tau p\cos\phi) = \frac{w}{g}\frac{dv}{dt} \text{ horizontally.}$$
 (2)

\* 'Roy. Soc. Proc.,' A, vol. 92, p. 329 (April 1, 1916).

The formal solutions of these equations are

$$t = \int_{\mathbf{B}}^{\mathbf{A}} \frac{w}{g\left(\mathbf{E}\tau p \sin \phi + w\right)} dv, \tag{3}$$

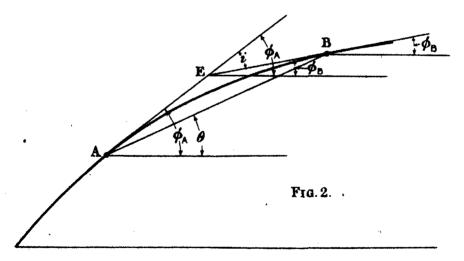
$$t = \int_{B}^{A} \frac{w}{g\left(\text{E}\tau p\cos\phi\right)} dv. \tag{4}$$

In these expressions p is a function of the velocity and  $\tau$  is a function of the height and is independent of the velocity. The equations cannot, therefore, be integrated as they stand, since  $\tau$  cannot be expressed as a function of v. The graphical method explained in my previous paper may, however, be applied step by step to get a solution in the following way:—

(1) Assume a value of the vertical velocity at B near enough to the given vertical velocity,  $v_A \sin \phi_A$ , at A to make the influence of the change of tenuity on the resistance negligibly small. Let  $v_B$  stand for the assumed value of the vertical velocity at B. Plot a curve representing the quantity

$$\frac{w}{g(\mathbf{E}\tau_{\mathbf{A}}p\sin\phi_{\mathbf{A}}+w)}\tag{5}$$

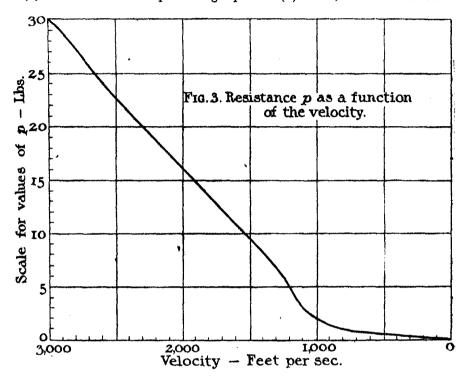
between the values of the given vertical velocity at A and the assumed value at B. In plotting this curve take  $\tau$  constant and equal to the tenuity at the height A. The resistance p is the only variable, and its value at a few points along the curve and the final point corresponding to



the assumed velocity is to be found by dividing the velocities selected by  $\sin \phi_A$  in order to reduce them to actual velocities in the trajectory, and then the corresponding values of p are taken either from a Table, or from a curve like the curve in fig. 3, drawn to a large scale. The error in the resistance

caused by assuming that  $\phi_A$  remains constant during the motion over this portion of the trajectory is negligibly small.

(2) From the curve representing equation (5) above, construct the corre-



sponding parts of the time-velocity and the time-height curves by the graphical method described in my previous paper.

- (3) From the diagram obtained in (2), measure off the height corresponding to the assumed vertical velocity at B, namely,  $v_B$ , and also the time-interval, and call the time-interval T. Equation (3) has now been solved, and also its derivative,  $h = \int_{B}^{A} v dt$ , on the assumption of constant tenuity. The solution gives—
  - (a) The vertical step in height y.
  - (b) The time-interval T corresponding to y.

We now go to equation (4), solving it in a similar way. The link connecting the two equations is the time-interval T. Elements of the time-velocity and the time-distance curves are constructed from assumed values of the horizontal velocities and an appropriate value of the tenuity, and then points are found on these elements corresponding to the time-

interval T, fixing at once the corresponding values of the horizontal step x and the horizontal velocity at the end of the step.

(4) Assume a few even values of the horizontal velocities, divide them by  $\cos \phi_A$  to get the corresponding values of the velocities in the trajectory, from which values of p are found for use in the expression

$$\frac{w}{g(\mathbf{E}\tau_1 p\cos\phi_{\Lambda})}.$$
 (6)

The value of  $\tau_1$  to be used in this expression is the average value during the step y. That is  $\tau_1 = (\tau_A + \tau_B)/2$ . Values of  $\tau_A$  and  $\tau_B$  can be found by calculation, or from a curve similar to that shown in fig. 7, where the tenuity is plotted as a function of the height. Generally, two values of (6) will be sufficient to determine the element of the auxiliary curve.

- (5) From the curve found in (4), construct the corresponding parts of the time-velocity time-distance curves by the general graphical method described in my previous paper.
  - (6) From the curves found in (5), measure off-
  - (c) The distance corresponding to the time-interval T.
  - (d) The velocity at the end of the time-interval T.

Then (c) is the horizontal distance x and (d) is the horizontal velocity at B.

(7) It remains to determine the direction of the tangent at B. Let the tangents to the trajectory through the points A and B (fig. 2) meet in E. Draw the chord AB. Then the angle EAB is equal to  $\phi_A - \theta$ . And it may be assumed, with negligible error, that the angle EBA is also equal to this. Then the exterior angle i is equal to  $2(\phi_A - \theta)$ , and the angle  $\phi_B$ , which the tangent at B makes with the horizontal, is given by

$$\phi_B = \phi_A - 2 (\phi_A - \theta). \tag{7}$$

The angle  $\theta$  in this expression is to be calculated from

, or

$$\tan \theta = y/x$$

using the values of y and x found respectively in (a) and (c).

(8) The velocity in the trajectory at B is given alternatively by

$$V_{B} = \frac{\text{the assumed vertical velocity at B}}{\sin \phi_{B}},$$
the determined harizontal velocity at

$$V_{B} = \frac{\text{the determined horizontal velocity at B}}{\cos \phi_{B}}.$$

These two should substantially agree and together furnish a check on the accuracy of the work.

(9) The initial conditions at B are now:-

Direction of the tangent  $\phi_B$ . Velocity along the tangent  $V_B$ . Tenuity  $\tau_B$  and the air resistance  $p_B$ .

All the data are therefore known for a fresh application of the method to find a point C on the trajectory.

Repeated applications of the method from point to point carry the trajectory up to the vertex, and then down again to any level which may be assigned. About eight points are sufficient to carry up to the vertex of the trajectory, and about six points bring it down to the ground again. Height to the vertex, and the range on the level or on any inclination, together with the time of flight, are then determined.

I made a first application of the method to the case of a shell weighing 380 lb., fired from a 9.2-inch gun elevated to 40°, taking a muzzle velocity 2375 feet per second, the data corresponding with one of the rounds fired from the 9.2-inch wire-wound gun used in the "Jubilee Trials" on June 12, 1888. The results obtained were: range 23,000 yards, and time of flight 70.65 seconds. The actual range and time of flight recorded in the reports of the trial are: range 20,236 yards, time of flight 63.5 seconds.

A study of the original report shows that there were difficulties which probably reduced the muzzle velocity. Allowing for this probable discrepancy between the muzzle velocity assumed, namely, 2375 feet per second, and the probably lower value which was actually obtained on the range, the agreement is good.

It may be noticed that, if the calculated range is reduced in the ratio of the observed time of flight to the calculated time of flight, the result gives a range very nearly equal to the observed range. Thus

$$\frac{23000 \times 63.5}{70.65} = 20,672$$
 yards.

The trajectory defined by 13 points found in the way described above, is shown in fig. 8 (p. 345). From this it will be seen that the greatest height is 6215 yards, and the striking angle or angle of descent is  $46\frac{1}{3}$ °.

The method of drawing a trajectory is illustrated in the following example by giving in detail the work of determining a point on this particular trajectory.

Example.

A shell weighing 380 lb. is fired at an angle of elevation of 40° with the horizontal, from a gun 9.2 inch diameter. The muzzle velocity is

2375 feet per second. The product of the coefficient of shape, k, and the coefficient of steadiness,  $\sigma$ , is 0.9. The value of the coefficient E is therefore  $0.9 \times 9.2^2 = 76.2$ .

Plot the trajectory, and from it find the height of the vertex above the level, the time of flight, and the range.

The resistance p is given by the curve fig. 3. The tenuity  $\tau$  is given as a function of the height by the curve fig. 7, and is also indicated in fig. 5. The sections following are numbered to correspond with those included in the explanation of the method given above.

The point A, fig. 4, is, for the first interval of the trajectory, the origin of the trajectory. The value of the tenuity  $\tau$  is unity, and the value of p corresponding to the muzzle velocity of 2375 feet per second is 21.03 lb.

At A the vertical velocity is  $V_A \sin \phi_A = 2375 \sin 40^\circ = 1525$  feet per second.

At A the horizontal velocity is  $V_A \cos \phi_A = 2375 \cos 40^\circ = 1820$  feet per second.

The Vertical Component y.—(1) Assume a vertical velocity at B of 1400 feet per second.

The value of the quantity (5) is calculated from

$$\frac{380}{32\cdot2\left(76\cdot2\times1\times p\sin 40^{\circ}+380\right)} = \frac{11\cdot8}{76\cdot2\times p\sin 40^{\circ}+380}.$$
 (8)

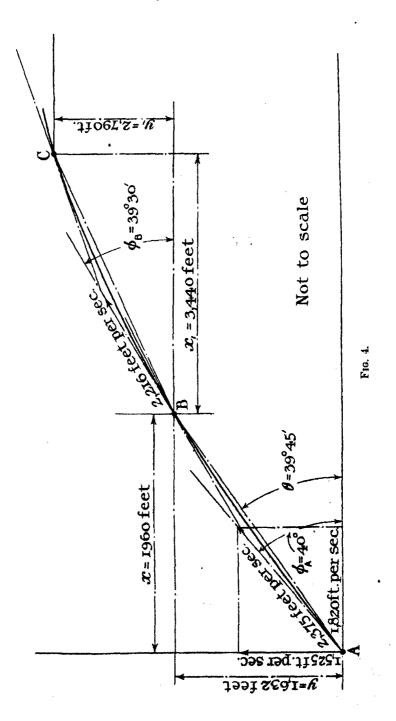
At A, where the velocity is 2375 feet per second, p = 21.03.

At B, where the assumed vertical velocity is 1400 feet per second, the corresponding velocity in the trajectory is  $1400/\sin 40^{\circ} = 2180$  feet per second, and the corresponding value of p is 18.49.

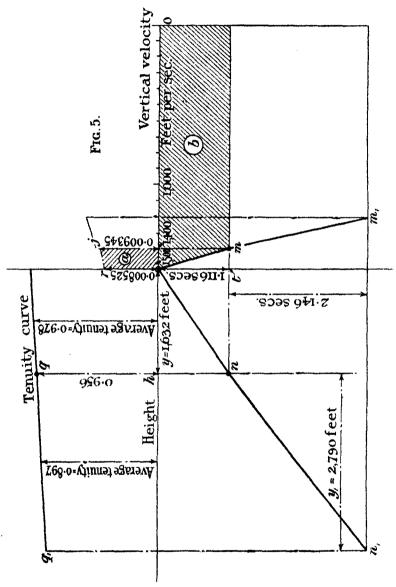
(2) The values of the quantity (5) at A and B respectively are 0.008525 and 0.009345. These are set up at the corresponding vertical velocities at Or and 1400-j (fig. 5). It is unnecessary to calculate intermediate values for the interval, so that r and j are joined by a straight line.

The area (a) represents the time taken for the vertical velocity to fall from the initial value, 1525, to the assumed value, 1400, and is, in fact, the solution of the differential equation (3) between the limits of the vertical velocities at A and B. The distance 1400-m represents this area, and m is therefore a point on the time-velocity curve, and 0m is the first element of the curve.

Again the area b represents the vertical distance moved through in the time Ot. The length tn is set out to scale to represent this distance, so that n is a point on the time-height curve, and On is the first element of the curve.



A vertical through n cuts the tenuity curve in q at the point where its value has fallen to 0.956.



(3) From this diagram (fig. 5), therefore,

Ot = 1.116 seconds is the time interval T,

Oh = 1632 feet is the vertical height y,

hq = the tenuity at the end of the interval = 0.956, and therefore the average value over the interval is 0.978.

The Horizontal Component.—(4) With the given data the quantity (6) becomes

$$\frac{11.8}{76\cdot2\,\tau_1p\cos\phi_A}\tag{9}$$

Assume 1700 an even value of the horizontal velocity.

The corresponding velocity in the trajectory is  $1700/\cos 40^{\circ} = 2219$  feet per second, for which p is found to be equal to 19. Inserting this value of p in (9), together with  $\tau_1 = 0.978$ , it reduces to 0.01086.

The value of (9) at A, calculated from p = 21.03 and  $\tau = 0.978$  and  $\phi_{\rm A} = 40^{\circ}$ , is 0.009875. Set these values up at the corresponding horizontal velocities (fig. 6), and two points, R and J, are determined on the auxiliary curve.

(5) The area (a) then represents the time for the horizontal velocity to change from 1820 to 1700; the distance 1700—M represents this area, and M is therefore a point on the time-velocity curve, and OM is the first element of the curve. Again the area (B) represents the horizontal distance moved through in the time Ot. The length tN is set out to represent this distance, so that N is a point on the time-distance curve and ON is the first element of the curve.

Now set down  $Ot_1$  to represent the time interval T = 1.116 second, found from fig. 5. Through  $t_1$  draw a horizontal to cut the curves, and through the points of intersection draw verticals cutting the distance axis in S and the velocity axis in 1710.

- (6) Scaling from the curves, OS = 1960 feet, and this is the co-ordinate x; and the velocity at v is 1710 feet per second, and this is the corresponding horizontal velocity at B.
  - (7) The direction of the tangent at B.

$$\tan \theta = \frac{y}{x} = \frac{1632}{1960}$$
, from which  $\theta = 39^{\circ} 45'$ ,

therefore

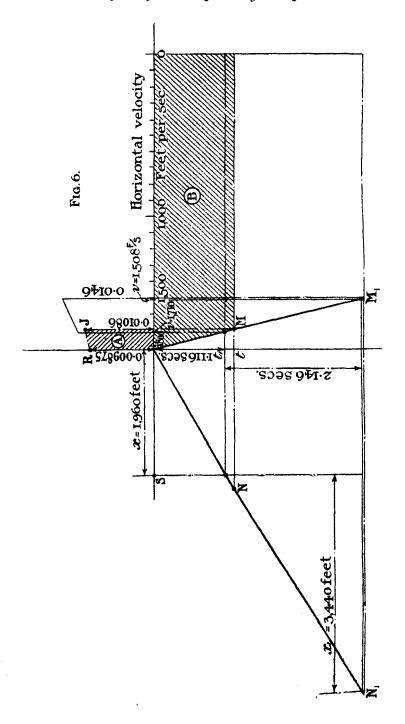
$$\phi_{\rm B} = 40^{\circ} - 2(40^{\circ} - 39^{\circ} 45') = 39\frac{1}{2}^{\circ}.$$

(8) The velocity in the trajectory at B is then

$$V_B = \frac{1400}{\sin 39\frac{1}{2}}$$
° = 2201 feet per second,

or alternatively 
$$V_B = \frac{1710}{\cos 39\frac{1}{2}}$$
 = 2216 feet per second,

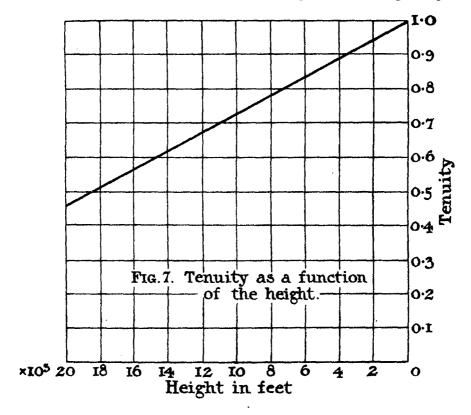
a sufficiently near agreement. Point B can now be plotted in fig. 4, and the direction of the tangent drawn in.



The data at B from which to construct the next element of the trajectory are now:—

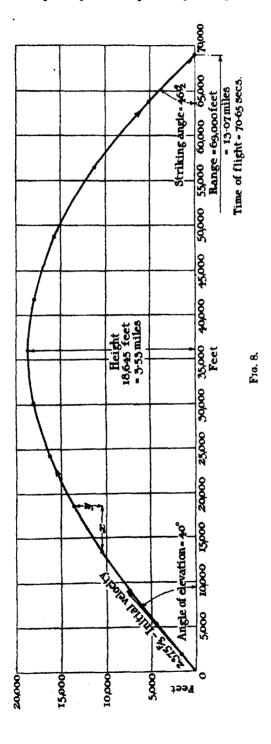
Velocity in the trajectory—2216 feet per second, Direction of the velocity—39½°, Tenuity—0.978.

The process is then repeated to get another point C. The second element  $mm_1$  of the time-velocity curve for the vertical component is shown in fig. 5, and also the second element  $nn_1$  of the time-height curve corresponding to



an assumed vertical velocity at C of 1200 feet per second. The time-interval corresponding to this step is 2.146 seconds, and the value of the tenuity is found by a vertical from  $n_1$  cutting the tenuity curve in  $q_1$ . Finally, the value of the vertical step  $y_1 = 2790$  feet.

The second elements  $MM_1$  and  $NN_1$  of the time-velocity and the time-distance curves for the horizontal component of the motion are shown in fig. 6, and the parts of these elements corresponding to the time-interval 2.146 seconds are  $x_1 = 3440$  feet, and the velocity at C is 1508 feet per



UPWARD

Vertical Components.

V, velocity in trajectory.	V sin φ.	Ang Ф		p.	τ. Average.	$\frac{11.8}{76.2rp \sin \phi + 380}.$	Time. T.	Distance.
ft./sec.	ft./sec.	0	′	lbs.	0.070	0.000	sec.	ft.
2875 2180	1525	40	0	21 ·03 18 ·49	0 ·978 0 ·978	0 :00852	1.110	1682
2201	1400 1400	40 89	80	18.75	0.897	0 ·00984 0 ·00987	1 .116	1082
1888	1200	39	30	14.65	0.897	0.01159	2 146	2790
1925	1200	88	36	15 16	0.885	0.01182	ar 140	2100
1604	1000	38	36	10.93	0.885	0 01450	2 .630	2893
1676	1000	36	86	11 .82	0.753	0.01540	_ 555	1 -550
1841	800	86	86	7 .15	0.758	0.01928	3 .463	8116
1485	800	88	52	8 .76	0.650	0.01900	1	
1076	600	38	52	2 .61	0.650	0 • 0 2 6 1 0	4.510	8157
1242	600	28	52	5 .66	0.540	0.02400		
830	400	26	52	1 '08	0.540	0.02940	5 .840	2670
1065	400	22	2	2 .44	0 .450	0.02870		i
584	200	22	2	0 .54	0.450	0.408050	5 920	1776
1000	200	11	28	1 '86	0.420	0.08015	_	1
0	0	11	28	0.0	0 420	0 .03100	6.115	611
			ĺ			Totals	31 .24	18,645

# Vertical Components.

DOWNWARD

V, velocity in trajectory.			ıgle. φ.	p.	τ. Average.	$\frac{11.8}{76.2\tau p \sin \phi - 380}$	Time. T.	Distance.
ft./sec.	ft./sec.	0	/	lbs.		The second secon	800.	ft.
0	0	0	0	0.0	0 488	0.08100		
200	200	0	0	0.111	0 .488	0.08100	6 200	620
945	200	12	171	1 .28	0.48	0 .08210	,	1
1880	400	12	171	14.54	0.48	0 .044.25	7 .685	2290
<b>96</b> 0	400	24	86 <del>1</del>	1 .675	0.614	0 '08400	}	1
1440	600	24	86 <u>î</u>	8 -85	0.614	0 .05685	9 085	4542
1020	600	35	581	1 .98	0.804	0.03825		1
1190	700	85	581	4 .98	0 .804	0.05880	9 .155	5950
1080	700	42	461	2 '08	0.940	0 .04200		1
Find fi	nal point					to give the	7 .340	5248
	total		tance	required.				
	300.00			- oq maroun		Totals	39 -415	18,645

second. The co-ordinates of the point C with reference to the point B, fig. 4, are therefore

 $y_1 = 2790$  feet,  $x_1 = 3440$  feet,

and the vertical and horizontal velocities at C are vertical, 1200 feet per second, as assumed, and horizontal, 1508 feet per second, as found by the process. Finally, the direction of the tangent at C is

#### FLIGHT.

Horizontal Components.

V, velocity in trajectory.	V сов ф.	Ang φ	gle.	p.	τ. Average.	$\frac{11.8}{76.2\tau p\cos\phi}.$	Time, T.	Distance
ft./sec.	ft./sec. 1820	40	, 0	lbs. 21 :08	0 -978	0 .00987	sec.	ft.
2010	1710	40	0	21 03	0.978	0.01075	1 -116	1960
2216	1710	89	30	19 01	0.897	0.01178	1 110	1300
22.0	1508.	89	30	19.01	0.897	0.01480	2 146	8440
1980	1508	38	36	15 24	0.835	0.01678	1	]
	1854	38	86	15 24	0.885	0.01890	2 .630	3686
1686	1854	86	36	11 .97	0.758	0.02140		
	1208	36	36	11 .97	0.758	0.02680	3 468	4414
1455	1208	33	52	9 ·12	0.650	0 '03150		{
	1088	88	52	9 12	0.650	0 -04300	4 510	5177
1242	1088	28	52	5 .66	0.540	0.05780		
	1012	28	52	5 •66	0.540	0 08180	5 .340	5607
1090	1012	22	2	2.70	0.450	0 ·13750		
	976	22	2	2 70	0 .450	0 16400	5 920	5900
1000	976	11	28	1 .86	0.420	0 · 20250		
	942	11	28	1 .86	0.420		6 · 115	5875
į	1					Totals	31 .24	36,059

### FLIGHT.

### Horizontal Components.

V, velocity in trajectory.	V cos φ.	1	ıgle. φ.	p.	7. Average.	$\frac{11.8}{76.2\tau p\cos\phi}.$	Time. T.	Distance
ft./sec.	ft./sec.	°	,	lbs.	0.499	0 :22500	B00.	ft.
942	942 916	o	0	1 ·57 1 ·57	0 ·438 0 ·438	0 24700	6 -200	- 5760
945	916 <b>882</b>	12 12	17±	1 ·58 1 ·58	0.48	0 ·20900 0 ·24300	7 .635	6864
970	882 880	24 24	361 361	1 ·675 1 · <b>675</b>	0.614	0 ·15500 0 ·19400	9 085	7776
1020	880 754	85 85	581	1 ·98 1 ·98	0 804	0 ·12040 0 ·15200	9 ·155	7250
<b>108</b> 0	754 695	42 42	461	2 '08	0 940	0 11055	7 .840	5808
						Totals	89 .415	32,958

$$\tan \theta = \frac{2790}{3440} = 0.811$$
, giving  $\theta = 39^{\circ} 3'$ ,

from which

$$\phi_{\rm C} = 39^{\circ} 30' - 2(39^{\circ} 30' - 39^{\circ} 3') = 38^{\circ} 36'.$$

The details of the whole calculation for the 13 points shown on fig. 8 are given in the annexed Table.

# The Dissipation of Energy in the Tides in Connection with the Acceleration of the Moon's Mean Motion.

By R. O. STREET, M.A., The University, Liverpool.

(Communicated by Sir Joseph Larmor, F.R.S. Received February 12, 1917.)

1. In the following paper an expression for the rate of dissipation of kinetic energy in a rotating sea is obtained in the form of an integral of a function of the surface-current velocities. This expression has been used to find an approximate value for the rate of dissipation in the Irish Sea, for which much tidal information is available, and the order of magnitude of the result obtained suggests that this direct effect of viscosity may account for at least an appreciable part of the earth's secular retardation.

The water is supposed of uniform density, and at the bed of the ocean to be relatively at rest. The motion, which, as usual, is regarded as small, is supposed non-turbulent, and simple-harmonic with respect to the time with a period of 12 hours. In actual tidal motion eddies are present, so that the result here obtained for the rate of dissipation may be regarded as a lower limit.

The question of stability is not considered. This would require a knowledge of the slight variations of density. It is frequently found\* that, at a given station, the maximum density is not at the bottom or the minimum not at the top.

The ordinary equations of hydrodynamics for a flat rotating sheet of water are applied to an element<sup>†</sup> of the ocean. Provided that the greatest linear dimension of the element is small compared with the radius of the earth, the error introduced is unimportant. In any element the bottom is supposed flat, and the linear dimensions are further restricted by the condition that, in the state of relative equilibrium, the depth, to a first approximation, is constant. As the results are obtained without introducing lateral boundary conditions, the method may be applied by summation to a region of any area.

- 2. Consider a plane element rotating with constant angular velocity  $\omega$  about a vertical axis, which is taken as the z co-ordinate axis, the bottom of the water being the plane z = 0. Let the x- and y-axes rotate in their
- \* Many examples of this are given in the Reports on the Hydrographical Investigations in the North Sea (North Sea Fisheries Investigation Committee).
- † The expression "element" is used to denote a portion of the ocean of such dimensions that the conditions here stated are satisfied within it.

plane with the given angular velocity  $\omega$ , and denote by U, V the velocities at time t, along and relative to these axes, of the particle of water which at that instant occupies the position (x, y, z). Then, if the conditions stated above are satisfied, and if the vertical acceleration of the water is neglected in comparison with g, the equations of relative motion may be written\*

$$\frac{\partial \mathbf{U}}{\partial t} - 2\omega \mathbf{V} = -g \frac{\partial}{\partial x} (\zeta e^{i\sigma t}) + \nu \Delta \mathbf{U} 
\frac{\partial \mathbf{V}}{\partial t} + 2\omega \mathbf{U} = -g \frac{\partial}{\partial y} (\zeta e^{i\sigma t}) + \nu \Delta \mathbf{V}$$
(1)

where  $\nu$  is the kinematic coefficient of viscosity,  $\Delta$  is the Laplacian operator  $\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$ , and

 $\zeta e^{i\sigma t} - \Pi/g \tag{2}$ 

is the elevation of the disturbed surface above its position of relative equilibrium, II being the disturbing potential.

If  $\Pi$  is proportional to  $e^{i\sigma t}$ , and  $\zeta$  is supposed a function of x, y only, let

$$(\mathbf{U}, \mathbf{V}) = (u, v) e^{i\sigma t}. \tag{3}$$

Then u, v are functions of x, y, z only, and the equations (1) become

$$\iota \sigma u - 2\omega v = -g \frac{\partial \zeta}{\partial x} + \nu \Delta u$$

$$\iota \sigma v + 2\omega u = -g \frac{\partial \zeta}{\partial y} + \nu \Delta v$$
(4)

For free motion in the absence of viscosity the elimination of  $\zeta$  between equations (4) and the equation of continuity leads to

$$\left(\Delta_1 + \frac{\sigma^2 - 4\omega^2}{gh}\right)(u, v) = 0, \tag{5}$$

where h is the depth of the water in the element, and  $\Delta_1$  is the operator  $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}$ . In free motion with  $\nu$  not zero the equations (5) will, of course, not be satisfied, but the right-hand sides will be functions of  $\nu$ ,  $\nu$ ,  $\nu$  which vanish with  $\nu$ . It may, therefore, be supposed that in a free oscillation of the sea

$$\Delta_1(u, v)$$
 and  $\frac{\sigma^2 - 4\omega^2}{gh}(u, v)$ 

are of the same order of magnitude.

If  $\Omega$  is the angular velocity of the earth's axial rotation, for an element of the sea in latitude  $\lambda$  the appropriate value of  $\omega$  is  $\Omega \sin \lambda$  or, say, 0.8  $\Omega$  for the neighbourhood of England. Also for a semi-diurnal oscillation  $\sigma = 2\Omega$ .

<sup>\*</sup> Lamb, 'Hydrodynamics,' §§206, 316.

<sup>+</sup> The validity of this supposition is verified later (§3).

Hence

$$\frac{\nu}{\sigma} \frac{\sigma^2 - 4\omega^2}{gh} = 0.72 \frac{\nu\Omega}{gh} = 9.6 \times 10^{-19}$$

for a depth of 1 metre, taking  $\nu = 0.018$  C.G.S. units.

It appears then that of the terms in u, v on the right-hand sides of equations (4) the parts  $v\Delta_1 u$ ,  $v\Delta_1 v$  are absolutely insignificant compared with the terms in u, v occurring on the left-hand sides of those equations. Thus the equations may be replaced by

$$\iota \sigma u - 2\omega v = -g \frac{\partial \zeta}{\partial x} + \nu \frac{\partial^2 u}{\partial z^2}$$

$$\iota \sigma v + 2\omega u = -g \frac{\partial \zeta}{\partial y} + \nu \frac{\partial^2 v}{\partial z^2}$$
(6)

Hence

$$\left(\frac{\partial^{2}}{\partial z^{2}} - \iota \frac{\sigma + 2\omega}{\nu}\right) (u + \iota v) = \frac{g}{\nu} \left(\frac{\partial}{\partial x} + \iota \frac{\partial}{\partial y}\right) \zeta$$

$$\left(\frac{\partial^{2}}{\partial z^{2}} - \iota \frac{\sigma - 2\omega}{\nu}\right) (u - \iota v) = \frac{g}{\nu} \left(\frac{\partial}{\partial x} - \iota \frac{\partial}{\partial y}\right) \zeta$$
(7)

The conditions to be satisfied by u, v are that there is no velocity at the bottom and no shearing stress at the free surface (supposed smooth). Hence

at 
$$z = 0$$
,  $u = v = 0$ ,  
at  $z = h$ ,  $\frac{\partial u}{\partial z} = \frac{\partial v}{\partial z} = 0$ .

The solution of the first of equations (7) is therefore

$$u + \iota v = \frac{\iota y}{\sigma + 2\omega} \left( 1 - \frac{\cosh\left\{ (h - z)\sqrt{\left[\iota(\sigma + 2\omega)/\nu\right]\right\}}}{\cosh\left\{ h\sqrt{\left[\iota(\sigma + 2\omega)/\nu\right]\right\}}} \right) \left( \frac{\partial}{\partial x} + \iota \frac{\partial}{\partial y} \right) \zeta. \tag{8}$$

Let 
$$(\sigma + 2\omega)/\nu = 2\alpha^2$$
,  $(\sigma - 2\omega)/\nu = 2\beta^2$ . (9)

Then with the values of  $\sigma$ ,  $\omega$ ,  $\nu$  used previously,  $1/\alpha = 12$  cm.,  $1/\beta = 35$  cm., so that if h is more than a few metres  $\tanh \alpha h$  and  $\tanh \beta h$  may be replaced by unity without appreciable error.

With these simplifications equation (8) becomes

$$u + \iota \nu = \frac{\iota g}{\sigma + 2\omega} \left\{ 1 - \dot{e}^{-\alpha(1+\iota)z} \right\} \left( \frac{\partial}{\partial x} + \iota \frac{\partial}{\partial y} \right) \zeta, \tag{10}$$

and in the same way from the second of equations (7)

$$u - \iota v = \frac{\iota g}{\sigma - 2\omega} \left\{ 1 - e^{-\beta(1+\iota)z} \right\} \left( \frac{\partial}{\partial x} - \iota \frac{\partial}{\partial y} \right) \xi. \tag{11}$$

Putting z = h, these equations give

$$u_0 \pm \iota v_0 = \frac{\iota g}{\sigma \pm 2\omega} \left( \frac{\partial}{\partial x} \pm \iota \frac{\partial}{\partial y} \right) \zeta \tag{12}$$

to the degree of approximation already used, where  $u_0$ ,  $v_0$  are the surface values of u, v, and all the upper or all the lower signs of the ambiguities are to be taken.

Combining equations (9), (10), (11), (12), the equation

$$\mathbf{U} \pm \iota \mathbf{V} = (u_0 \pm \iota v_0) (1 - \exp\{-z\sqrt{[\iota(\sigma \pm 2\omega)/\nu]}\}) e^{\iota \sigma t}$$
 (13)

is obtained for the complex relative velocities U, V.

3. It is now possible to verify the assumption that in a sea with viscous quality

$$\Delta_1(u,v)$$
 and  $\frac{\sigma^2-4\omega^2}{gh}(u,v)$ 

are of the same order of magnitude.

The equation of continuity for free motion is now

$$\iota \sigma \zeta = -\int_{0}^{h} \left( \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} \right) dz. \tag{14}$$

Integrating both sides of equations (10), (11) with respect to z and neglecting  $e^{-ah}$ ,  $e^{-\beta h}$  as before,

$$\int_{0}^{h} (u+\iota v) dz = \frac{\iota y h}{\sigma + 2\omega} (1+A) \left( \frac{\partial}{\partial x} + \iota \frac{\partial}{\partial y} \right) \zeta$$

$$\int_{0}^{h} (u-\iota v) dz = \frac{\iota y h}{\sigma - 2\omega} (1+B) \left( \frac{\partial}{\partial x} - \iota \frac{\partial}{\partial y} \right) \zeta,$$

$$A\alpha = B\beta = (\iota - 1)/2h. \tag{15}$$

where

Hence from equation (14)

$$2\iota\sigma\zeta = -\int_0^h \left\{ \left( \frac{\partial}{\partial x} - \iota \frac{\partial}{\partial y} \right) (u + \iota v) + \left( \frac{\partial}{\partial x} + \iota \frac{\partial}{\partial y} \right) (u - \iota v) \right\} dz$$
$$= -\iota g h \left( \frac{1 + A}{\sigma + 2\omega} + \frac{1 + B}{\sigma - 2\omega} \right) \Delta_1 \zeta.$$

Therefore

$$\left(1 + \frac{\sigma - 2\omega}{2\sigma} \mathbf{A} + \frac{\sigma + 2\omega}{2\sigma} \mathbf{B}\right) \Delta_1 \zeta + \frac{\sigma^2 - 4\omega^2}{gh} \zeta = 0.$$
 (16)

By equations (15) the coefficient of  $\Delta_1 \zeta$  differs from unity by a small quantity proportional to  $i^{\frac{1}{2}}$ .

From equations (10), (11) it follows that u, v are also solutions of equation (16), so that

$$\Delta_1 u + rac{\sigma^2 - 4\omega^2}{gh} u$$
 and  $\Delta_1 v + rac{\sigma^2 - 4\omega^2}{gh} v$ 

are each nearly equal to -1; and the assumption that they are of the same order of magnitude as unity is justified.

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It is important to notice that since, by equations (10), (11),

$$\frac{\partial^2}{\partial z^2} (u \pm \iota v) = \frac{\sigma}{\nu} \exp\left[-\left\{\frac{\alpha}{\beta}\right\} (1 + \iota)z\right] \left(\frac{\partial}{\partial x} \pm \iota \frac{\partial}{\partial u}\right) \zeta,$$

 $\nu \partial^2 u/\partial z^2$  and  $\nu \partial^2 v/\partial z^2$  do not contain a factor proportional to a power of  $\nu$ .

4. If (p, q, r) denote the real relative velocities of the particle of water at (x, y, z) the rate of dissipation of energy in the element is

$$\iiint \Phi \, dx \, dy \, dz,$$

integrated through the volume considered, where

$$\Phi = \mu \left\{ 2 \sum \left( \frac{\partial p}{\partial x} \right)^{2} + \sum \left( \frac{\partial r}{\partial y} + \frac{\partial q}{\partial z} \right)^{2} \right\},\,$$

 $\mu$  being the coefficient of viscosity. For oceanic tidal waves the important terms in  $\Phi$  are

$$\mu\left\{\left(\frac{\partial p}{\partial z}\right)^2 + \left(\frac{\partial q}{\partial z}\right)^2\right\}.$$

Integrating by parts with regard to z, the rate of dissipation per unit surface area is found to be

$$-\mu \int_0^h p \left( \frac{\partial^2 p}{\partial z^2} + q \frac{\partial^2 q}{\partial z^2} \right) dz, \tag{17}$$

the integrated part vanishing at both limits.

Writing

$$u = u_1 + \iota u_2, \qquad v = v_2 + \iota v_2$$

where  $u_1$ ,  $u_2$ ,  $v_1$ ,  $v_2$  are real, there follows from equation (3)

$$U = (u_1 \cos \sigma t - u_2 \sin \sigma t) + \iota (u_1 \sin \sigma t + u_2 \cos \sigma t).$$

Hence

$$p\frac{\partial^{2}p}{\partial z^{2}} = (u_{1}\cos\sigma t - u_{2}\sin\sigma t)\frac{\partial^{9}}{\partial z^{2}}(u_{1}\cos\sigma t - u_{2}\sin\sigma t),$$

of which the mean value over a whole period is

$$\frac{1}{2}\left(u_1\frac{\partial^2 u_1}{\partial z^2} + u_2\frac{\partial^2 u_2}{\partial z^2}\right). \tag{18}$$

The mean rate of dissipation of energy per unit surface area is therefore, from equation (17), given by

$$F = -\frac{1}{2}\mu \int_0^h \left\{ u_1 \frac{\partial^2 u_1}{\partial z^3} + u_2 \frac{\partial^2 u_2}{\partial z^2} + v_1 \frac{\partial^2 v_1}{\partial z^3} + v_2 \frac{\partial^2 v_2}{\partial z^3} \right\} dz$$
$$= -\frac{1}{2}\mu \int_0^h \mathbf{R} \left\{ u \frac{\partial^2 u'}{\partial z^2} + v \frac{\partial^2 v'}{\partial z^3} \right\} dz$$

where R denotes "the real part of," and u', v' are the conjugate complexes of u, v. Hence

$$\mathbf{F} = -\frac{1}{4}\mu \int_0^h \mathbf{R} \left\{ (u+\iota v) \frac{\partial^2}{\partial z^2} (u'-\iota v') + (u-\iota v) \frac{\partial^2}{\partial z^2} (u'+\iota v') \right\} dz. \quad (19)$$

Let  $u_0 + \iota v_0 = P$ ,  $u_0 - \iota v_0 = Q$ , and let P', Q' be the conjugate complexes of P, Q. Then from equations (10), (12)

$$u + \iota v = P\{1 - e^{-a(1+\iota)z}\}$$
  
$$u' - \iota v' = P'\{1 - e^{-a(1-\iota)z}\}.$$

Therefore

so that

$$\int_0^h \mathbf{R} \left\{ (u+\iota v) \frac{\partial^2}{\partial z^2} (u'-\iota v') \right\} dz$$

$$= -2 \mathbf{P} \mathbf{P}' \alpha^2 \int_0^h \mathbf{R} \left\{ [1 - e^{-\alpha(1+\iota)z}] \iota e^{-\alpha(1-\iota)z} \right\} dz$$

$$= -2 \mathbf{P} \mathbf{P}' \alpha^2 \int_0^h \mathbf{R} \left\{ \iota e^{-\alpha(1-\iota)z} \right\} dz$$

$$= -2 \mathbf{P} \mathbf{P}' \alpha \mathbf{R} \left\{ \iota / (1-\iota) \right\} \quad \text{approximately}$$

$$= -\mathbf{P} \mathbf{P}' \alpha$$

Hence from equation (19)

$$F = \frac{1}{4}\mu \left\{ PP' \sqrt{\left(\frac{\sigma + 2\omega}{2\nu}\right) + QQ' \sqrt{\left(\frac{\sigma - 2\omega}{2\nu}\right)} \right\}}$$

or, since  $\mu = \nu \rho$ , where  $\rho$  is the density of the water,

$$F = \frac{1}{8}\rho\sqrt{(2\nu)}\left\{PP'\sqrt{(\sigma+2\omega)} + QQ'\sqrt{(\sigma-2\omega)}\right\}. \tag{20}$$

Let 
$$u_0 = \mathbf{U}e^{i\theta}, \quad v_0 = \mathbf{V}e^{i\phi}$$
 (21)

where  $\mathbf{U}$ ,  $\mathbf{V}$ ,  $\theta$ ,  $\phi$  are real functions of x, y. Then the components of the relative surface velocities, being the real parts of

$$\mathbf{U}_{\ell^{\iota(\theta+\sigma t)}}, \quad \mathbf{V}_{\ell^{\iota(\phi+\sigma t)}}$$
are
$$\mathbf{U}\cos(\theta+\sigma t), \quad \mathbf{V}\cos(\phi+\sigma t). \tag{22}$$

The hodograph of the motion is thus an ellipse,\* whose dimensions and orientation are functions of the position of the point on the surface.

Changing the origin of time, the component velocities may be written

$$\mathbf{U}\cos(\sigma t'+\psi), \quad \mathbf{V}\cos(\sigma t'-\psi)$$

where  $2\psi = \theta - \phi$ .

If therefore W is the resultant relative surface velocity

$$\begin{aligned} 2\mathbf{W}^{2} &= \mathbf{U}^{2} + \mathbf{V}^{2} + \mathbf{U}^{2} \cos 2(\sigma t' + \psi) + \mathbf{V}^{2} \cos 2(\sigma t' - \psi) \\ &= \mathbf{U}^{2} + \mathbf{V}^{2} + (\mathbf{U}^{2} + \mathbf{V}^{2}) \cos 2\psi \cos 2\sigma t' - (\mathbf{U}^{2} - \mathbf{V}^{2}) \sin 2\psi \sin 2\sigma t' \\ &= \mathbf{U}^{2} + \mathbf{V}^{3} + (\mathbf{U}^{4} + \mathbf{V}^{4} + 2\dot{\mathbf{U}}^{2}\mathbf{V}^{2} \cos 4\psi)^{3} \cos (2\sigma t' + \chi), \text{ say.} \end{aligned}$$

<sup>\*</sup> For drawings of the ellipses at several stations, see "Hydrographical Observations in the North Sea," in the 'Bulletin Hydrographique,' 1910-11, 1912-13 (Conseil International pour l'Exploration de la Mer).

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Hence, if W, w are the maximum and minimum values of  $\mathbf{W}$ ,

$$W^{2} + w^{2} = \mathbf{U}^{2} + \mathbf{V}^{2}$$

$$Ww = \mathbf{U}\mathbf{V}\sin 2\psi = \mathbf{U}\mathbf{V}\sin (\theta - \phi)$$
(23)

It is convenient to suppose that W is always positive, w may then be negative.

Now  $PP' = |u_0 + \iota v_0|^2$  $= (\mathbf{U}\cos\theta - \mathbf{V}\sin\phi)^2 + (\mathbf{U}\sin\theta + \mathbf{V}\cos\phi)^2$  $= \mathbf{U}^2 + \mathbf{V}^2 - 2\mathbf{U}\mathbf{V}\sin(\theta - \phi).$ 

Hence  $PP' = (W - w)^2$  and similarly  $QQ' = (W + w)^2$ . (24)

Thus from equation (20) the mean rate of dissipation of energy per unit surface area is given by

$$F = \frac{1}{6}\rho \sqrt{(2\nu)} \{ (W - w)^2 \sqrt{(\sigma + 2\omega)} + (W + w)^2 \sqrt{(\sigma - 2\omega)} \}.$$
 (25)

Actual measurements of current velocities show that w is usually very small compared with W, so that it might, without serious error, be put equal to zero. It is, however, easy to show that, whatever value w may have, the order of magnitude of F is unaltered by neglecting w.

With the values of  $\sigma$  and  $\omega$  used before

$$\sqrt{(\sigma+2\omega)} = \sqrt{(3.6\Omega)}, \qquad \sqrt{(\sigma-2\omega)} = \sqrt{(0.4\Omega)}.$$

Hence F is proportional to

 $3(W-w)^2 + (W+w)^2$  $W^2 - Ww + w^2$ .

or to

Denote this expression by f(w). Then the maximum and minimum values of f(w) are respectively  $3W^2$  and  $\frac{3}{4}W^2$ , since w must lie between -W and W. Also  $f(0) = W^2$ . Thus f(w) must lie between  $\frac{3}{4}f(0)$  and 3f(0), and is therefore always of the same order of magnitude as f(0).

Writing w = 0,  $\sigma = 2\Omega$ ,  $\omega = \Omega \sin \lambda = \Omega \cos \theta$ , where  $\lambda$  is the latitude and  $\theta$  the co-latitude of the place considered, equation (25) gives

$$F = \frac{1}{4}\rho W^2 \sqrt{(\nu\Omega)} \{ \sqrt{(1 + \cos\theta)} + \sqrt{(1 - \cos\theta)} \},$$
or
$$F = \frac{1}{2}\rho W^2 \sqrt{(\nu\Omega)} \cos \frac{1}{2}\lambda.$$
(26)

The Rate of Dissipation of Energy in the Main Fairway of the Irish Sea at the Time of Spring Tides.

5. The expression obtained in equation (26) for the mean rate of dissipation of energy by viscosity per unit surface area has been applied

to that portion of the Irish Sea which may be described as the Main Fairway. The boundary of the area used has been determined approximately, so that all regions in which the range of tide is more than about one-tenth of the depth have been excluded. The boundary so obtained follows the coastline fairly closely, except in Liverpool Bay and between Walney Island and the Isle of Man. The unit of area taken for the purpose of summation is bounded by meridians at an interval of 15' and parallels at an interval of 10'. On a Mercator chart of this region such a unit is approximately square. In each of these units (or occasionally in a portion of a unit) a value is assigned to the maximum surface-current velocity, and the corresponding rate of dissipation is evaluated.

The values of these maximum velocities at a large number of stations are given in the Admiralty manual, 'The Tides and Tidal Streams of the British Islands.' These, supplemented in a few cases by values taken from their chart of the Irish Sea, enable a value of W<sup>2</sup> to be interpolated in each of the units used. As the observed velocities are given in knots and quarter-knots, it is convenient to express W<sup>2</sup> in (½ knots)<sup>2</sup>.

In the few cases in which the boundary of the region precludes the use of the whole of a unit, the value of  $W^2$  has been reduced proportionately. The

South boundary			West	t bounds	ry of un	it (West	Longitu	de).		and an artist of the state of t
of unit (North Latitude).	6° 15′	6°	5° 45′	5° 80'	5° 15′	5°	4° 45′	4° 30′	4° 15′	4.º
<b>55° 10′</b> 0		256 144	100 100	36 49	0 1 abc					
54° 50′ 40 89 20 10 0		64 bed	49 25 bod 8 b	49 81 82 ba 18 ba 4 ba	75 a 100 25 4 4	144 68 8ad 8ad	144 30acd	196	100 81	82 ad 82 ad
53° 50′ 40 30 20 10 0		16 16 8ed	4 4 25 64 81 169	0 4 25 81 100 121	1 49 86 121 121 121	64 64 64 144 96 100	81 64 121 49acd 16abd 49	49 49 144	49 49 81	86 49 81
52° 50′ 40 30 20 10	72 bc 100 144 144	196 b 196 100 100 121 121	196 169 121 100 121 100	144 169 144 100 100 196	144 169 144 100 100 147 d	144 169 100 64 64 16acd	8 a b 86 64 16			

Mean Values of W2 in the Units of Area.

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letters a, b, c, d following a number in the Table\* denote that the N.E., N.W. S.W., S.E. quarters of the unit have not been included.

The area of the unit depends on its position, and to a sufficient approximation is equal to  $150\cos\lambda$  square nautical miles,  $\lambda$  being the mean latitude of the unit. Without appreciable error the portion of the sea considered may be divided into four regions:  $52^{\circ}$  N.— $53^{\circ}$  N.,  $53^{\circ}$  N.— $54^{\circ}$  N.,  $54^{\circ}$  N.— $55^{\circ}$  N.— $55^{\circ}$  N., within each of which one value of  $\lambda$  is used.

From the Table of values of W<sup>2</sup> the following summary of results has been constructed:—

Mean latit	ade (λ).	xW³.	ΣW <sup>2</sup> cos λ cos ½λ.	Number of units (N).	N cos λ.
52° 8	30'	4412	2406	354	21.76
58 8	30	2766	1469	40	28 .80
54 8	30	1366	705	201	11 .76
55 1	lo l	686	847	71	4 14

Thus

$$\Sigma W^2 \cos \lambda \cos \frac{1}{2}\lambda = 4927$$
$$\Sigma N \cos \lambda = 61.46$$

where the summation now extends over the whole of the main fairway of the Irish Sea.

Taking  $\rho = 64$ ,  $\nu = 1.4 \times 10^{-6}$ ,  $\Omega = \pi/(12 \times 60^2)$  in foot-pound-second units, equation (26) gives as the mean rate of dissipation of energy over the whole area considered

$$5.1 \times 10^9$$
 foot poundals per second. (27)

The area within which this dissipation takes place is 150  $\Sigma N \cos \lambda$ .

6. Neglecting the relatively small vertical velocity, the kinetic energy of the disturbed motion is

$$\frac{1}{2}\rho \int_0^h (p^2+q^2) dz \text{ per unit surface area}$$

$$= \frac{1}{2}\rho \int_0^h \{(u_1\cos\sigma t - u_2\sin\sigma t)^2 + (v_1\cos\sigma t - v_2\sin\sigma t)^2\} dz.$$

Hence, if T denotes the mean value of this kinetic energy taken over a whole period,

$$T = \frac{1}{4}\rho \int_0^h (u_1^3 + u_2^3 + v_1^2 + v_2^3) dz$$

$$= \frac{1}{8}\rho \int_0^h \{(u + \iota v)(u' - \iota v') + (u - \iota v)(u' + \iota v')\} dz.$$
(29)

<sup>\*</sup> The publication of this Table has been sanctioned by the Hydrographer.

Now

$$\int_0^h (u+\iota v)(u'-\iota v') dz$$

$$= \operatorname{PP'} \int_0^h \{1-e^{-\alpha(1+\iota)z}\} \{1-e^{-\alpha(1-\iota)z}\} dz$$

$$= \operatorname{PP'} \int_0^h 1-2e^{-\alpha z}\cos\alpha z + e^{-2\alpha z}\} dz$$

$$= \operatorname{PP'} \left(h-\frac{1}{2\alpha}\right) \text{ to the approximation already used}$$

$$= \operatorname{PP'} h \qquad \text{very nearly.}$$

Hence from equation (29)

$$T = \frac{1}{8}\rho h (PP' + QQ'),$$

so that from equations (24)

$$T = \frac{1}{4}\rho h (W^2 + w^2). \tag{30}$$

A rough approximation to the mean kinetic energy of the portion of the Irish Sea already considered may be obtained by supposing h and  $W^s + w^s$  constant, and equal to 250 feet and 5 (knots) respectively over the whole 9220 square nautical miles. With these assumptions equation (30) gives for the mean kinetic energy

$$9 \times 10^{15}$$
 foot-poundals. (31)

Owing to the action of external forces, this mean kinetic energy is nearly constant over long periods of time. Suppose that in the absence of these forces it could be expressed by an equation of the form

$$K = K_0 e^{-t/\tau}$$

so that  $\tau$  is the period in which the mean kinetic energy would be reduced in the ratio e to 1. Then

$$\tau = \mathbf{K} + \left( -\frac{\partial \mathbf{K}}{\partial t} \right)$$

$$= 1.8 \times 10^6$$
 seconds,

or about two hours, using the figures in (27), (31).

For a non-rotating sea of uniform depth, the approximate formula of Hough\* is, in the present notation,

$$\tau = h \sqrt{\frac{2}{\sigma \nu}}$$
$$= 5 \times 10^6 \text{ seconds.}$$

using the same values of  $\sigma$ ,  $\nu$ , h as before.

\* 'London Math. Soc. Proc.,' vol. 28, p. 275 (1897).

The agreement between these two values of  $\tau$  is as close as could have been expected.

#### The Effect of Tidal Friction on the Earth's Axial Rotation.

7. About three-quarters of the earth's surface is covered by water; so that if energy were dissipated throughout all the oceans at the same rate per unit surface area as in the Irish Sea, the mean rate of dissipation due to tidal friction would be

$$6 \times 10^{18}$$
 foot-poundals per second. (32)

This value is probably several times too high, as in general much smaller current velocities are observed in the large expanses of water than in the confined regions of the Irish Sea.

8. It is well known that observations of the moon's position indicate an acceleration\* in its orbital motion referred to terrestrial time units. This acceleration might be explained by assuming that the earth's axial rotation has a retardation of about 4' of arc per century per century.

If T is the kinetic energy of the earth's rotation, and I is its moment of inertia, then

$$T = \frac{1}{2} I \Omega^2$$

so that

$$\frac{1}{T}\frac{\partial T}{\partial t} = \frac{2}{\Omega}\frac{\partial \Omega}{\partial t}.$$

Let  $-\partial\Omega/\partial t$  correspond to the retardation of 4' per century per century. Then

$$-\frac{1}{T}\frac{\partial T}{\partial t} = \frac{8}{60 \cdot 360} (100^{9} \cdot 365^{9} \cdot 24 \cdot 60^{9})^{-1}$$

where the second is the unit of time. Taking  $T = 5 \times 10^{30}$  foot-poundals, the rate of decay of energy is given by

$$-\frac{\partial \mathbf{T}}{\partial t} = 1.6 \times 10^{13} \text{ foot poundals per second.}$$
 (33)

It will be seen that this rate of dissipation is about one-quarter that given in equation (32). No agreement of the two results except in orders of magnitude could have been expected.

- 9. It is interesting to find the maximum surface-current velocity (assumed uniform over all the oceans) which will give rise to the retardation of 4' per century per century in the earth's rotation.
- \* The actual amount of this irregularity is a matter of controversy, but its order of magnitude is of the quantity used here. For references, cf. Sir J. Larmor, 'M. N. R. Astron. Soc.,' vol. 75, p. 211 (1915). It is there shown that if the interaction between the earth and the moon is considered, any loss of energy is divided between the two bodies in the ratio 14:1.

If the maximum velocity at every point is W, and if at any latitude the area of the land is a third that of the sea, the mean rate of dissipation of energy would be, from equation (26),

$${}_{4}^{8}\pi\rho\,\mathrm{W}^{2}\mathrm{R}^{2}\sqrt{(\nu\Omega)}\int_{-\frac{1}{2}\pi}^{\frac{1}{2}\pi}\cos\frac{1}{2}\lambda\cos\lambda\,d\lambda=\pi\rho\,\mathrm{W}^{2}\mathrm{R}^{2}\sqrt{(2\nu\Omega)}$$

where R is the radius of the earth. Hence from equation (33)

$$W^2 = \frac{1.6 \times 10^{18}}{\pi \rho \, R^2 \sqrt{(2\nu\Omega)}},$$

or

$$W = 2$$
 feet per second = 1.2 knots.

My thanks are due to Sir J. Larmor for the interest he has taken in the work, and to Dr. Proudman for help and advice on many points which have arisen.

The Complete Photo-electric Emission from the Alloy of Sodium and Potassium.\*

By WILLIAM WILSON, Ph.D.

(Communicated by Prof. O. W. Richardson, F.R.S. Received February 17, 1917.)

The experimental work described in the present paper suggested itself to the writer in connection with an earlier investigation<sup>†</sup> on the law governing the temperature variation of the complete photo-electric emission from a hot body, i.e. the photo-electric emission from a body in equilibrium with the full (black body) radiation corresponding to its temperature. By making use of hypotheses contained in the quantum theory, the writer obtained the following expression for the current per unit area

$$C = AT(1 + 2kT/\phi + 2k^2T^2/\phi^2)e^{-\phi/kT}$$

where  $\phi$  is the work done in removing an electron from the hot body, and is equal to  $h\nu$ ,  $\nu$  being the lowest frequency of the radiation capable of producing a photo-electric emission, and h being Planck's constant. The quantity k is the "gas constant" reckoned for one molecule, and A is a quantity independent of T, and characteristic of the substance. As the expression inside the brackets in the above formula does not differ appreciably from unity, the latter is substantially of the same type as Richardson's equation  $C = AT^{\lambda}e^{-\phi/kT}. \tag{1}$ 

$$C = AT^{\lambda}e^{-\phi/kT}, \tag{1}$$
\* The expenses of this research were partly defrayed by the aid of a grant from

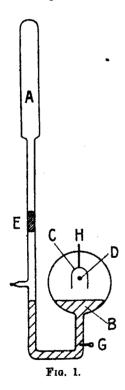
the Government Grant Committee of the Royal Society, to whom my thanks are due.

<sup>+</sup> W. Wilson, 'Annalen der Physik,' vol. 42, p. 1154 (1913).

for the thermionic emission. Richardson\* has also shown that it follows, from thermodynamic considerations, that this law governs the complete photo-electric emission. There is reason to believe that the thermionic emission is not wholly photo-electric in origin,† but it is clear that some portion of it is the complete auto-photo-electric emission of the substance concerned, and that the law governing its temperature variation should be the same as that for the whole thermionic emission. We are thus led to expect that, when a body is exposed to an external source of full radiation, the same law will govern the variation of its complete photo-electric emission with the temperature of the source of the radiation. This expectation has been confirmed by experiments on the alloy of sodium and potassium, the description of which constitutes the subject of the present paper.

Description of the Apparatus and Experimental Arrangements.

The part of the apparatus containing the alloy is illustrated by figs. 1



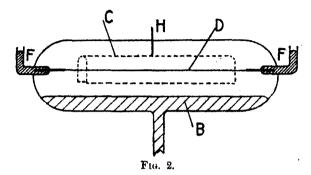
and 2. It consisted of a glass vessel completely sealed up and without taps, many previous attempts to prepare the alloy, and introduce it in satisfactory condition, having failed on account of the great difficulty of getting sufficiently good stop-cocks. sodium and potassium, in atomic proportions, were introduced into the portion A (fig. 1). This was afterwards sealed on to the rest of the apparatus, which was kept inverted during the preparation of the alloy, and not as actually shown in the figure. The naphtha, in which the metals were immersed, was run off as far as possible before the apparatus was finally closed. The vessel was then evacuated by a Toepler pump and a charcoal tube immersed in liquid air. The metals were then melted, and the alloy formed, by applying a Bunsen flame to the exterior of the tube. After the apparatus had been evacuated as completely as possible, it was sealed off from the pump, and the alloy run through a plug of glass wool E, and brought into the position B (figs. 1 and 2) by inverting the whole vessel, so that the liquid filled the U-shaped portion. About 3 cm. above the surface of the alloy was a

horizontal platinum wire D (figs. 1 and 2), about 9 cm. in length

<sup>\* &#</sup>x27;Phil. Mag.,' vol. 23, pp. 619 and 620 (1912).

<sup>†</sup> See a paper by O. W. Richardson, 'Phil. Mag.,' vol. 31, p. 149 (1916).

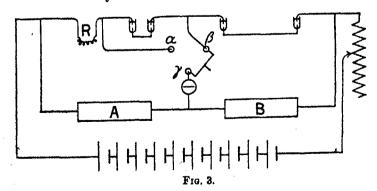
and 0.2 mm. in diameter. The ends of this wire were fused on, by means of gold, to thicker platinum leads sealed into mercury tubes FF (fig. 2).



Surrounding the wire, but not actually touching it, was a shield of silver foil C (figs. 1 and 2). This was slightly open at the lower side, to allow the radiation from the platinum wire to reach the alloy. This arrangement of silver shield and platinum wire constituted an approximately full radiator.

A battery of 8 or 10 accumulators was used to heat the wire of the radiator, and, at the same time, the connections were so arranged that the wire and its leads constituted one arm of a Wheatstone bridge (see fig. 3), the remaining arms consisting of a resistance R of 2.016 ohms of thick eureka or platinoid wire immersed in paraffin oil, and the two large resistances (of the order of 4000 ohms) contained in a good post-office box. In addition to these four resistances, a fifth one was connected with the bridge. This consisted of a very short piece of the same wire as that of the radiator, and was furnished with mercury tubes and leads exactly similar to those of the radiator wire.

The whole arrangement is shown in fig. 3. By means of the mercury cups,  $\alpha$ ,  $\beta$ , and  $\gamma$ , one of the terminals of the bridge galvanometer could be connected in such a way that the short wire and its leads could be included



in the radiator arm of the bridge, or, when desired, in the arm containing R. By this means the resistance of a uniformly hot portion of the wire of the radiator could be found. If this resistance be denoted by x, and that of the leads and colder ends of the wire by  $\eta$ , we can determine x from the equations

$$\frac{a}{b} = \frac{R}{2\eta + x}, \qquad (\alpha \gamma)$$

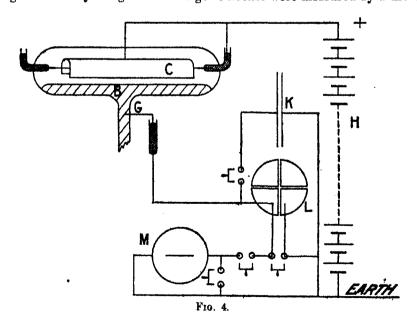
$$\frac{a'}{b'} = \frac{R + \eta}{\eta + x}, \qquad (\beta \gamma)$$
(2)

where a and b are the resistances in the arms A and B, when the mercury cups  $\alpha$  and  $\gamma$  are connected; a' and b', the corresponding resistances when  $\beta$  and  $\gamma$  are joined.

The bridge galvanometer was of the moving coil type, and had a resistance of, approximately, 100 ohms. The whole arrangement was very sensitive; in fact, such errors as may have entered into the measurements cannot be ascribed to the individual bridge measurements, since a change of 1 in 4000 or 5000 of the arms A and B produced an easily discernible galvanometer deflection.

#### Measurement of the Photo-electric Current.

The methods employed to measure the photo-electric current from the alloy, when subjected to the radiation from the hot wire radiator, are shown diagrammatically in fig. 4. The larger currents were measured by a moving



coil galvanometer (fig. 4, M), which gave a scale deflection of 1 cm. for  $1437 \times 10^{-8}$  ampères, and was provided with a shunt, so that its sensitiveness could be reduced, when desired, to one-eighth of this. One terminal of the galvanometer was "earthed," and the other (fig. 4) could be connected with the alloy by means of a platinum wire G, sealed in the glass.

The radiator wire (or one end of it) and the shield C could be maintained at a fixed positive potential by means of a battery of 240 small dry cells (fig. 4, H), the negative pole of which was "earthed." The smaller photoelectric currents were measured by means of an electrometer L and a condenser K. The capacity of the latter could be varied from 0.001 microfarad to 0.3 microfarad to suit the requirements of individual measurements.

The sensitiveness of the electrometer amounted to nearly 16 cm. scale deflection for 1 volt. The currents were measured by taking the time required by the electrometer and condenser to charge up to the potential represented by a deflection of 10 cm. on the scale. The sensitiveness of the electrometer was determined immediately before and after use. The condenser, electrometer, the part of the apparatus containing the alloy and radiator, and all the connections were enclosed in metal boxes and tubes, which were all connected to the same "earth" as the negative pole of the high-tension battery.

## The Saturation of the Currents.

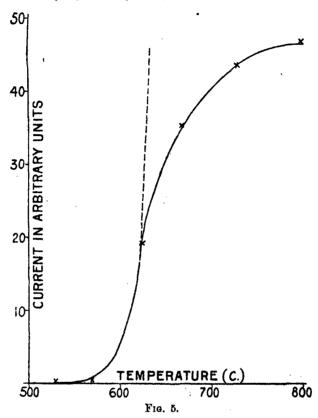
A number of measurements were carried out for the purpose of ascertaining what potential would saturate the currents. The form of the apparatus and the comparatively large magnitude of the currents rendered it necessary to use a relatively high potential for this purpose. In fact, the upper limit of the photo-electric currents, which could be satisfactorily measured, was largely determined by the voltage available for saturating them.

The dependence of the photo-electric current on the temperature of the radiator, when an insufficiently high voltage was maintained between the alloy and radiator, is illustrated by fig. 5, which is plotted from actual measurements. The ordinates represent the currents in arbitrary units, and the abscissæ approximate temperatures. The applied potential was 100 volts.

It will be seen that the current increases rapidly with the temperature up to a certain point, beyond which it rises less and less rapidly, and ultimately becomes stationary. This phenomenon is already well known, and is explained by the fact that at the higher temperatures the emission is very large and the applied potential is not sufficiently high for saturation, owing to the mutual repulsion of the emitted electrons. This kind of effect was first observed by J. E. Lilienfeld,\* who accounted for it along lines similar to

<sup>\* &#</sup>x27;Phys. Zeitschrift,' vol. 9, p. 193 (1908).

the above. It has also been considered by C. D. Child,\* and at greater length, more recently, by I. Langmuir.†

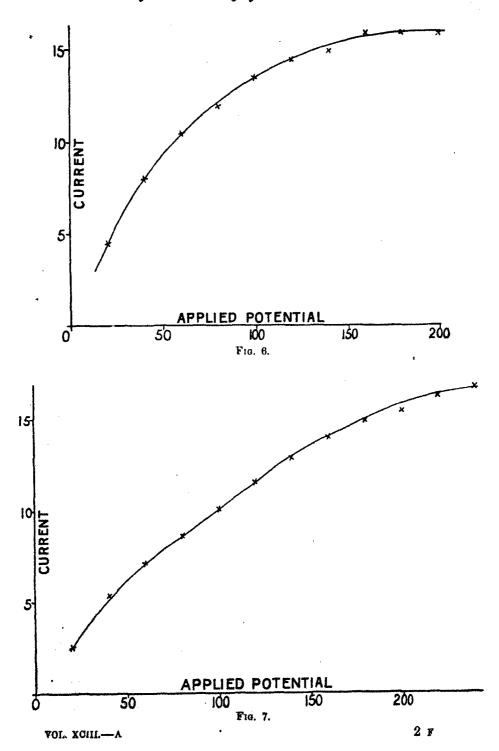


In fig. 6 is shown the dependence of the current on the applied potential when the radiator temperature was 573° C. The abscissæ will represent volts when multiplied by 1.46. The current, as will be seen from the figure, is practically saturated with 200 volts. In the actual measurements described below, the applied potential was 350 volts, so that the currents obtained with the temperature stated above, and with all lower temperatures, were undoubtedly saturated. Higher radiator temperatures were employed, but the saturation of the currents was less satisfactory.

The saturation curve corresponding to a radiator temperature of 624° C. is shown in fig. 7. In this case saturation appears to be just reached at the highest potential at my disposal, namely, 350 volts. (The abscissæ in fig. 7 have to be multiplied by 1.46 to give volts.) It is possible that the current

<sup>\* &#</sup>x27;Phys. Rev.,' vol. 32, p. 492 (1911).

<sup>† &#</sup>x27;Phys. Rev.,' vol. 2, p. 453 (1913).



measured, when the highest radiator temperature (669° C.) was used, is slightly below the saturation value, but is not likely that it is much below, since the point corresponding to it in fig. 9 is not much below the straight line on which the other points may be approximately said to lie.

#### The Positive Emission from the Radiator Wire.

The experimental method described above precludes any possibility of errors due to a negative thermionic emission from the radiator wire, since the direction and magnitude of the applied potential were such as to effectually prevent any negative ions, which might be emitted from the radiator, from reaching the alloy. It is, however, obvious that any positive emission will be included in the currents measured by the galvanometer or electrometer. The silver shield, although it could be insulated from the wire, was useless as a means of testing or allowing for a possible remanent positive emission from the latter, since the heating process, necessary to get rid of this emission, was associated with some condensation of metallic vapour on the shield. It was therefore necessary to subject the wire for a prolonged period to a considerably higher temperature than those employed for the measurements of the complete photo-electric emission. During this heating a positive potential was applied to the wire, as the writer and other investigators\* have observed that the rate of decay of the positive emission is dependent on the applied potential.

When the final measurements of the complete emission were carried out, the wire had been heated one or two hours a week over a period of about three months, and during these measurements the phenomenon of decay was This fact indicates that the positive leak, included in the measured currents, was of negligible magnitude. Before the prolonged heating, the decay characteristic of the positive emission was very marked. An accidental circumstance enabled an upper limit to be assigned to any positive emission included in the currents which are regarded as photoelectric ones. During the earliest heating of the radiator wire, the latter emitted a small quantity of gas. This showed itself by a small, but easily observable, movement of the alloy in the U-shaped bend, and also by attacking the alloy. A thin layer, showing the colours of thin films, formed over the alloy surface. This had the effect of greatly reducing the ordinary photo-electric emission from the alloy. When it was in this condition the currents observed were much smaller than those ultimately measured under the same conditions, but with a renewed alloy surface, and after the

<sup>\*</sup> W. Wilson, 'Phil. Mag.,' vol. 21, p. 634 (1911). See also O. W. Bichardson, 'The Emission of Electricity from Hot Bodies,' p. 227 et seq.

positive emission and decay had been got rid of. In some of the earliest series of measurements, currents as low as  $2 \times 10^{-8}$  ampères were observed with a radiator temperature of  $669^{\circ}$  C.; whereas with the same temperature and a clean alloy surface, and after long heating of the radiator wire, but otherwise similar conditions, the current rose to  $48 \times 10^{-8}$  ampères. These numbers show that the positive leak was less than 1/24 of the total current observed during the final series of measurements, and as the radiator wire was heated till the decay ceased to be perceptible, it may be safely assumed that it was practically absent.

It may be mentioned here that the direct thermionic emission from the alloy, which was undoubtedly heated to some extent by the radiation falling on it, did not contribute sensibly to the measured currents. This was established by maintaining the radiator at the highest temperature employed in the experiments for a sufficiently long period to give the alloy at least as high a temperature as any it could have during the actual photo-electric measurements. No emission from the alloy could be detected with the galvanometer after the current in the radiator wire had been switched off. Had the thermionic contribution been only 1/150 of the total emission from the alloy it could easily have been detected.

#### Final Measurements and Results.

The measurements of the complete photo-electric emission from the Na-K alloy are given in Table I. Four fiducial temperatures were employed for determining the temperatures of the radiator. These were:—

Melting point of potassium sulphate, 1070° C.

Melting point of sodium chloride, 801° C.

Melting point of lead chloride, 447° C.

Melting point of naphthalene, 80° C.

The corresponding "platinum" temperatures were calculated by means of Callendar's formula,

$$t-t_p = 1.5 \{ (t/100)^2 - t/100 \},$$

where t is the temperature (Centigrade) and  $t_p$  the "platinum" temperature. A small crystal of each substance was placed on a radiator wire, and the resistance of the wire (less leads and cold ends) determined when it was just hot enough to melt the crystal. These resistances and the "platinum" temperatures of the corresponding melting points are given in Table II:

Current in radiator wire.	(αγ.)		$(\beta\gamma)$ .		Galvano-	Electrometer measurements.		
	<b>A</b> .	В.	A.	В.	meter deflections.	Deflections.	Time.	Capacity
ampères.					em.	em.	B00.	mf.
2.8	4000	2417	4000	1694	8 -4*			1
2 .25	4000	2876	4000	1660	5 .05*	į		1
2 .20	4000	2806	4000	1626	1 -90#	1		1
2 15	7000	3957	7000	2780	7 -40+	1		1
2 ·10	7000	<b>\$850</b>	7000	2720	2 20+			1
2 .05	7000	3744 "	7000	2660	0.70+			1
2 00	7000	<b>3</b> 650	7000	2600		10	78	0.8
1 -95	7000	8554	7000	2536		10	92 .5	0.1
1.90	7000	8480	7000	2487		10	76	0.08
1.85	7000	3874	7000	2417		10	87 -2	0.01
1.80	7000	3294	7000	2357		10	58	0.003

Table I.

Note.—An electrometer deflection of 15.55 cm. represents 1.02 volts. A and B are the resistances in ohms of the corresponding bridge arms (fig. 3).  $(\alpha\gamma)$ ,  $(\beta\gamma)$  indicate that the corresponding mercury cups were connected.

Table II.

Substance.	Melting point.	Resistance.
Potassium sulphate	914	0 •9580
Sodium chloride	717	0 .7990
Lead chloride	425	0 .5461
Naphthalene	80	0 2674

These measurements are very consistent with one another, as will be seen from fig. 8. The "platinum" temperatures, corresponding to the measurements given in Table I, were calculated by means of the formula

$$\alpha t_p + \beta - x = 0, \tag{3}$$

where  $t_p$  is the "platinum" temperature, and x the resistance of the wire. For the constants,  $\alpha$  and  $\beta$ , the following values, deduced from the fiducial data in Table II, were employed:—

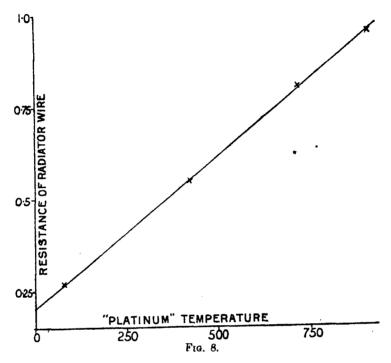
$$\alpha = 0.0008253, \quad \beta = 0.2005.$$

The calculated results are given in Table III. Column 2 contains the resistance of the radiator wire (corresponding to different temperatures) as calculated by equations (2) from the measurements in Table I. In column 3

<sup>\* 1</sup> cm. =  $8 \times 1.487 \times 10^{-8}$  ampère.

<sup>† 1</sup> cm. =  $1.437 \times 10^{-8}$  ampère.

are the corresponding "platinum" temperatures obtained by equation (3) and the values of  $\alpha$  and  $\beta$  given above. The Centigrade temperatures computed



by Callendar's formula are in column 4. The remaining four columns contain, respectively, the absolute temperatures, their reciprocals, the common

Table III.

Heating current in radiator wire.	Resistance of radiator wire, less that of leads and cold ends.	tp.	t.	T.	T <sup>1</sup> × 10 <sup>4</sup> .	log <sub>io</sub> C.	log <sub>10</sub> C/T <sup>2</sup> .
ampères.	ohms.						
2.8	0 7062	612 -7	,609	942	10.615	7 9849	12 .0868
2 · 25	0 :6874	589 <b>-</b> 9	642	915	10 .029	7 7689	13 8411
2 ·20	0 .6749	57 <b>4</b> ·8	624	897	11 148	7 8894	13 4888
2 · 1.5	0 6544	5 <b>49 ·9</b>	594	867	11 .584	7 0968	13 1507
2 10	0.6401	582 ·6	578	846	11 ·8 <b>2</b> 0	8.5000	14 .6452
2.05	0 6258	515 .8	558	826	12 107	8 .0026	14 1667
28.00	0.6102	496 4	581	804	12 438	9 -8990	15 5885
1 95	0 .5981	475 .7	507	780	12 .821	10 8405	15 0503
1 90	0.5802	460 · I	488 5	761 .6	13 123	TO 3848	16 5215
1.85	0 .5620	488 0	468	786	18 -587	II ·7696	18 0858
1.80	0.5449	417 -8	440	718	14 025	11 ·8166	17 6104

logarithms of the photo-electric currents and the common logarithms of the photo-electric currents divided by the squares of the absolute temperatures.

In order to test the validity of equation (1), which represents the expected relation between the complete photo-electric emission and the temperature of the radiator, it is convenient to put in the following form:—

$$\log \frac{C}{T^{\lambda}} = \log A - \frac{\phi}{k} \left(\frac{1}{T}\right), \tag{4}$$

from which it will be seen that there is a linear relationship between log C/T<sup>\*</sup> and 1/T. These two quantities are plotted in fig. 9 from the results given in

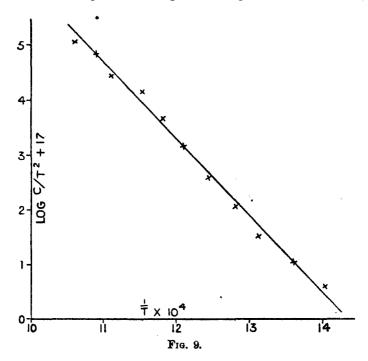


Table III ( $\lambda$  being taken to be 2). The points, as will be seen, lie very close to a straight line over the whole of the very wide range of the photo-electric currents given in the Table. The logarithm of the largest current exceeds that of the smallest by 4.668 approximately, so that the extreme values of the currents differ by a factor of 46600.

The tangent of the angle, under which the straight line in fig. 9 meets the horizontal (1/T) axis, is to a close approximation 4/3, and therefore, by equation (4)

$$\frac{\phi}{k} = \frac{4 \times 10^4}{3 \times 0.4343},$$

where 0.4343 is  $\log_{10} e$ . The entropy constant k is known to be  $1.34 \times 10^{-16}$  ergs per degree, so that we get

$$\phi = \frac{4 \times 1.34}{3 \times 0.4343} \times 10^{-12} \text{ ergs},$$
i.e.,  $\phi = 4.02 \times 10^{-12} \text{ ergs},$ 
or  $\phi = 4.02 \times 10^{-19} \text{ joules}.$ 

For the purpose of comparison with thermionic or other measurements of  $\phi$ , it will be convenient to give its value in equivalent volts. The charge on an electron is very near

 $1.57 \times 10^{-19}$  coulombs.

and therefore we find for the drop of potential equivalent to \$\phi\$

$$V = \frac{4.02 \times 10^{-19}}{1.57 \times 10^{-19}}$$
 joules per coulomb,

i.e. 
$$V = 2.56$$
 volts.

This result is in satisfactory agreement with the corresponding quantity as determined by Richardson from thermionic measurements on sodium,\* his value being 2.65 volts. It should be said, however, that Prof. Richardson considers that his measurements may be subject to considerable errors through lack of saturation and the possible occurrence of chemical effects.

We can deduce the threshold frequency from the value of  $\phi$  given above, that is to say, the lowest frequency of the radiation which is capable of causing a photo-electric emission. This is simply effected by the equation

$$\phi = h\nu$$

which is based on the quantum theory. The quantity h is Planck's constant and may be taken to be

$$6.5 \times 10^{-27}$$
 erg × sec.

The remaining quantity  $\nu$  is the threshold frequency. We have, therefore,

$$\nu = \frac{4.02 \times 10^{-12}}{6.5 \times 10^{-27}} \, \text{sec.}^{-1},$$

$$\nu = 6.2 \times 10^{-14} \text{ sec.}^{-1}$$

This corresponds to a wave-length (in air) of

or

$$\lambda = 485 \mu\mu$$

approximately. Richardson and Compton+ find for sodium

$$\lambda = 587 \,\mu\mu$$
 or  $\nu = 5.2 \times 10^{-14} \,\text{sec.}^{-1}$ .

- \* O. W. Richardson, 'Emission of Electrons from Hot Bodies,' p. 69.
- † O. W. Richardson and K. T. Compton, 'Phil. Mag.,' vol. 24, p. 585 (1912).

Millikan\* finds for the same metal

$$\lambda = 680 \,\mu\mu$$
 or  $\nu = 4.41 \times 10^{-14} \,\text{sec.}^{-1}$ .

There is no reason to suppose that \(\lambda\) is smaller for the Na-K alloy than for sodium. The explanation of the discrepancies in the numbers just given lies in the fact, illustrated by the curves relating to sodium, in a paper by Richardson and Compton, that & (and therefore the threshold frequency) is a function of the state of oxidation of the surface of the metal. The writers just mentioned (loc. cit.), although they worked with a good vacuum, noticed a well marked "fatigue." They found, for example, that the photo-electric currents measured 21 hours after the formation of the fresh sodium surface were considerably smaller than those measured only one hour afterwards. The present writer also noticed the "fatigue" phenomenon, which is, of course, very well known. After the formation of a new alloy surface, the photo-electric current for a given radiator temperature diminished for some time, but soon reached a stationary value, so that the same current could be measured days afterwards, provided the same radiator temperature was employed. Though the alloy surface appeared perfectly clean and bright (and remained so), there is no doubt that, during the time which had to elapse before a series of measurements could be carried out, a very thin film of oxide formed over the surface, so that  $\phi$  acquired a somewhat greater value than that corresponding to a perfectly clean surface.

#### Conclusion.

The law governing the variation of the complete photo-electric emission from the alloy of sodium and potassium, with the temperature of the source of radiation, has been experimentally investigated, and found to be well expressed (as, indeed, theoretical considerations suggest it should be) by Richardson's formula for the temperature variation of the thermionic emission from metals.

I wish to take this opportunity of expressing my thanks to Prof. O. W. Richardson for his valuable advice, and for the interest he has taken in this investigation.

<sup>\*</sup> Millikan, 'Phys. Rev.,' vol. 7, p. 380 (1916).

<sup>†</sup> O. W. Richardson and K. T. Compton, 'Phil. Mag.,' vol. 26, p. 563 (1913).

### Experiments with Mercury Jets.

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Section I.—The Relation between the Jet-length and the Velocity of Efflux.

1. Introductory.—Certain electro-chemical experiments, to be described in a subsequent communication, arose out of peculiarities which we noticed in the behaviour of a stream of mercury issuing from the lower, drawn-out, end of a vertical tube containing that liquid. The salient feature of the phenomena is the relation between the length of the continuous part of the liquid stream, called for convenience the "jet-length," and the "head" under which the mercury is ejected.

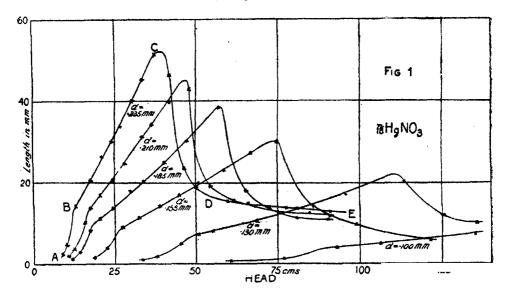
The experiments were made with orifices of diameters varying from about 0.25 mm, downwards to about 0.1 mm. It was found that the relation between the jet-length l and the head h depended appreciably upon the form of the nozzle through which the mercury escaped. For definiteness the nozzles were all constructed in the same way, namely by drawing out a piece of capillary tubing of about 1 mm, bore and severing it, as nearly as possible perpendicularly, at the centre of the constricted part. The nozzle so obtained tapered, in between 1 and 2 cm., from the original diameter of the tube to the diameter of the orifice and was very nearly cylindrical at the point of discharge. The values of the jet-length were determined by means of a cathetometer microscope.

2. General Features of the lh Curves for Jets of Different Diameters and Constant Surface Tension.—In the particular experiments represented in fig. 1, the mercury fell into a solution of mercurous nitrate (of strength 0.1 grm.-mol. per litre) contained in a vessel with flat glass sides. The object of using this solution was to ensure that the surface tension of the mercury should be practically constant throughout the measurements.

Considering the curve ABCDE, of the figure, which refers to an orifice of diameter 0.235 mm., it will be seen that between A and B, where the heads are at first only just sufficient to cause the jet to form, the jet-length increases very rapidly as the head rises. At B the rate of increase of l with h changes suddenly, becoming smaller and remaining practically constant till C is reached. Beyond this point the jet-length falls, very rapidly at first, as the head is increased. At the higher heads (near E) the rate of decrease of jet-length is comparatively small. Between C and D the jet is relatively unstable,

lengthening and shortening in a capricious way which makes definite measurements of its length difficult. Sometimes it is impossible to obtain anything more than rough values of its mean length.

It will be seen that the other jets give lh curves of the same character as



that just described. In each case there are two critical points at which the value of dl/dh changes suddenly. The critical jet-lengths decrease and the critical heads rise as the diameter of the orifice diminishes.

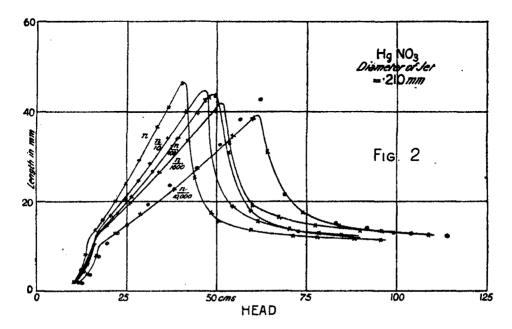
3. The lh Curves for Jets of Constant Diameter and Different Surface Tensions.—In order to find how the positions of the critical points depended upon the surface tension we made the observations represented in fig. 2 with an orifice of 0.21 mm, diameter.

The different curves were obtained using solutions of HgNO<sub>8</sub> of different strengths, it being known that the surface tension between mercury and a solution of HgNO<sub>8</sub> decreases as the salt-content rises. The points marked by circles (①) were obtained when distilled water was used. It will be noticed at once that, although the critical jet-length does not alter greatly, the critical head rises as the surface tension increases.

4. Critical Velocities of Efflux.—It is sufficient for the experiments referred to in §1 that the phenomena exhibited in figs. 1 and 2 exist; but they are of some general interest and we have therefore endeavoured to verify certain impressions as to their cause.

The sudden drop in the jet-length at the higher critical point reminded us of the experiments of Osborne Reynolds dealing with the critical velocity of flow of a liquid through a pipe. It seemed likely that there might be similar critical velocities for jets of the kind we used.

In order to test this impression we performed some qualitative experiments with a water jet into which, along its axis, was fed a thin column of red ink.



This jet gave *lh* variations resembling those of figs. 1 and 2 and the ink remained a thin stream along the axis until the upper critical head was reached. Immediately after this was passed, turbulent motion became obvious. The ink was dispersed throughout the jet.

We could not, of course, perform similar experiments with the mercury; but, although the water jet was comparatively very wide, it seemed reasonable to suppose that the higher critical point had the same cause in both cases. We were, therefore, led to regard the peculiar behaviour of the jets as due to the existence of critical velocities. From this point of view it seemed likely that the lower critical velocity was the counterpart of the phenomenon observed by Allen\* in connection with the motion of spheres through liquids.

5. Theoretical Relation between the Variables upon which Critical Velocities Depend.—If, in the case of a pipe, we suppose the only variables involved to be its diameter d and the viscosity  $\mu$  and density  $\rho$  of the liquid, we can (as

is well known) deduce a relation between the critical velocity and the variables by the method of dimensions. The result is

$$v_c \propto \mu (\rho d)^{-1}$$

where  $v_c$  is the critical velocity.

In the case of a jet, however, we have a free surface and therefore an additional variable, the surface tension of the liquid, upon which the critical velocities may depend. Introducing this factor into the dimensional equation we now get

$$v_{\sigma} \propto \sigma^{x} \mu^{1-2x} (\rho d)^{x-1}$$

where  $\sigma$  is the surface tension and x is an undetermined index.

If we accept this result we see that x must be positive since, from fig. 2, we find that  $v_c$  increases with  $\sigma$ . Also, since, from fig. 1,  $v_c$  increases as d diminishes, x-1 must be negative. Therefore the value of x must lie between zero and unity.

This is as far as we can go without further experimental data, unless, for example, we assume that the viscosity, if it has any influence, must tend to increase the critical velocity. In that case we might draw the further conclusion that 1-2x must be positive and therefore that x cannot exceed  $\frac{1}{2}$ .

6. Experimental Relation between the Critical Velocity and the Diameter of the Jet.—The velocities of the jet were not determined in the experiments of fig. 1; but in another set of measurements (in which the mercury fell into distilled water) the upper critical velocities were determined approximately. The following Table contains the results:—

Diameter of orifice.  d.	Critical head.	Critical velocity.	$\frac{v\sqrt{d}}{1000}$ .
em.	cm,	cm./sec.	•
0.0127	111.5	280	25 9
0.0172	77	223	29
0 <b>·020</b> 2	54	188	26 .7
0 0248	42	170	26 8
0 .0295	39	145	25

Measurements of this kind cannot be made very accurately because very slight disturbances are sufficient to alter considerably the head under which the jet breaks down and it is of course impossible to guarantee that the orifices are of strictly similar character. But the experiments obviously suggest that the critical velocity is inversely proportional to the square root of the diameter, i.e., that  $x = \frac{1}{2}$ .

7. Experimental Relation between the Oritical Velocity and the Surface Tension.—Another approximate estimate of x can be made by means of the

results shown in fig. 2. The ratio of the surface tensions of the n and n/1000 solutions of HgNO<sub>3</sub> was measured and found to be nearly 1.3. The upper critical velocities for these solutions were not determined at the time, but from subsequent observations it can be inferred that their ratio was not far from 1.15. Hence, since  $\sqrt{1.3} = 1.14$ , the value  $x = \frac{1}{2}$  again comes into view.

8. The Physical Significance of the Results.—These results suggest that the viscosity of the liquid has little influence upon the critical velocities and that, to a first approximation at any rate, we may write

$$v_c \propto (\sigma/\rho d)^{\frac{1}{2}}$$
.

If we put this in the form

$$\rho v_c^2 \propto \sigma/d$$

we see at once, without recourse to the method of § 5, that it is dimensionally correct. For, as is well known, both quantities have the dimensions of pressure. The first term suggests the operation of "inertia" forces; the second the opposing influence of the pressure due to surface tension. We return to this later on. We may, however, remark here that we should not expect the relation to be universally true. Its simplicity must arise from the fact that, in particular cases, the "inertia" forces are predominant. There are probably other cases in which, for example when the viscosity is large, "viscous" forces are no longer negligible.

9. Lord Rayleigh's Theory of Liquid Jets .- The quantities called "critical velocities" in the preceding paragraphs are not accompanied by any perceptible discontinuities in the relation between the velocity of efflux and the head; the changes in the jet-length are the only indication of their existence. We therefore turned our attention next to the consideration of the factors which determine the length of the jet, and have endeavoured to apply Lord Rayleigh's theory to the results which we have obtained. This theory\* develops the consequences of the fact, first noticed by Plateau and applied by him to the explanation of Savart's results, that a cylindrical liquid column is unstable when its length exceeds its circumference. It follows from this fact that any disturbance impressed upon the liquid column at the orifice will, if its wave-length exceeds the circumference of the column, increase in amplitude as it travels downwards until, finally, the sides of the column will come together and the continuity of the jet will be destroyed. The time which elapses before this occurs will depend upon the initial amplitude of the disturbance and upon the rate at which that amplitude grows.

<sup>\* &#</sup>x27;Proc. Lond. Math. Soc.,' vol. 10, p. 4 (1878).

If a is the initial amplitude,  $a_0$  the value which it has to acquire before disintegration occurs, and t the time required, we may suppose these connected by an equation of the form

$$a_0 = ae^{qt}$$

$$t = \frac{1}{a} \log_e a_0/a,$$

or

Whence, if we knew the value of q and of a for any given disturbance, we could calculate the value, l = vt, which the jet-length would have for a given velocity v (supposed constant) of descent of the liquid.

It is easy to show by the method of dimensions that, if viscosity be neglected, we must have

$$q \propto 1/t \propto \sqrt{(\sigma/\rho d^3)}$$
.

Lord Rayleigh has further shown that the exact result is of the form

$$q = f(x) \cdot \sqrt{(\sigma/\rho d^8)}$$

where  $x = \lambda/\pi d$  is the ratio of the wave-length of the disturbance to the circumference of the jet, and that q has a well-defined maximum value occurring near x = 1.44.

For equal amplitudes, therefore, a disturbance of wave-length  $\lambda = 1.44 \times \pi d$  will cause disintegration more rapidly than any other. Moreover, if we considered disturbances of unequal initial amplitudes  $a_1$  and  $a_2$ , for which the values of q were  $q_1$  and  $q_2$ , the times  $t_1$  and  $t_2$  required by them to produce disintegration would be connected by the equation

$$t_2 = t_1 + (q_1 - q_2)t_1/q_2 - 1/q_2 \cdot \log_e a_2/a_1$$

whence, for  $q_1 > q_2$ , we should have  $t_2 > t_1$  even with  $a_2 > a_1$  if we had  $(q_1 - q_2)t_1 > \log_e a_2/a_1$ .

Hence, if the times of disintegration were long enough, the disturbance with the greatest q would produce disintegration sooner than any other.

Without exact knowledge of the initial disturbance of the jet, we can imagine it resolved into components of different wave-lengths and amplitudes, whose effects are superposed, and can suppose that the relation between the wave-lengths and amplitudes of these components determines the conditions under which the jet breaks down.

The time of disintegration will be given by

$$a_0 = ae^{ty\sqrt{(\sigma/\rho d^2)}}$$

where a is the initial amplitude of the disintegrating disturbance, and y is the value of f(x) with which its wave-length corresponds.

Substituting l/v for t we get

$$l = v \cdot 1/y \cdot \log a_0/a \cdot \sqrt{(\rho d^3/\sigma)}$$

as the simplest theoretical relation between the variables with which we are concerned.

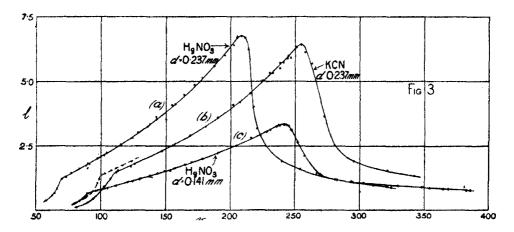
10. The Difference between our Results and those of Savart in Terms of this Theory.—For our jets, unlike those of Savart, in which the liquid (water) flowed through a hole, several millimetres in diameter, in the bottom of a containing vessel, the value of l/v was not even approximately constant.

We may take this to mean that, in our case, the quantity  $1/y \cdot \log \alpha_0/\alpha$  was variable and may assume that the variation was probably confined to  $\alpha$ .

The experiments of which the results are collected in fig. 3 were made, primarily, to test more closely the truth of the relation

$$v_c \propto \sqrt{(\sigma/d)}$$

suggested by the experiments of figs. 1 and 2.



In this figure the values of l (in cm.), for certain cases, are plotted against the values of v (in cm. per sec.). The latter were determined by weighing the amounts of mercury which escaped through the nozzle in measured times, and by dividing the volumes escaping per second by the cross-sectional area of the orifice. The error introduced by this method of calculation is not great because, in consequence of their shortness in comparison with their initial velocity, our jets (unlike those of Savart which were very much longer) were nearly cylindrical. Except at the lowest velocities they did not taper perceptibly. The calculated velocity probably represents, within one or two per cent., the mean velocity of the jet.

In experiments (a) and (b) the diameter of the jet was 0.2365 mm.; in experiment (c) it was 0.141 mm. In (a) and (c) the solution was n/4 HgNO<sub>3</sub>; in (b) it was n/4 KCN.

The curves are, of course, of the same general character as the *lh* curves of figs. 1 and 2.

11. Application of the Theory to Account for the Form of the lv Curve.—
From the final expression in § 9, assuming y constant, we get

$$\frac{dl}{dv} = \frac{1}{y} \cdot \sqrt{\frac{\rho d^3}{\sigma}} \left\{ \log \frac{a_0}{a} - \frac{v}{a} \cdot \frac{da}{dv} \right\}.$$

From this we see that the form of the first part of the lv curve can be accounted for if we assume da/dv to be negative when v is small, i.e., if we suppose the initial amplitude of the disintegrating disturbance decreases at first as the velocity of efflux rises.

We can explain the second part if the value of da/dv changes suddenly at the first critical point. Just beyond this point dl/dv is seen to be roughly equal to l/v. The interpretation of this would be that here da/dv is practically zero. At higher velocities it becomes appreciably negative again and remains of this sign until the second critical point is reached. Here, in order to explain the third part of the curve, we have to assume that da/dv acquires, comparatively suddenly, a large positive value.

We could form a picture of this sequence of events by imagining that the incipient turbulence appearing at the first critical point is just sufficient, at that point, to counteract the tendency of the amplitude to decrease as the velocity rises. The fuller turbulence appearing at the higher critical point is, on the other hand, great enough to cause a large increase in the amplitude of the initial disturbance and a corresponding decrease in the length of the jet.

12. More Accurate Determination of the Relation between the Form of the lv Curve and the Value of the Surface Tension.—The experiments (a) and (b) were to be used to test whether the relation

$$v_1/v_2=\sqrt{(\sigma_1/\sigma_2)}$$

connects the critical velocities  $v_1$  and  $v_2$  when  $\sigma$  varies and d is constant.

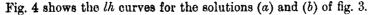
We chose solutions of HgNO<sub>8</sub> and of KCN for our purpose because it was desirable that the surface tensions should be (1) easily comparable, (2) as different as possible, and (3) as free as possible from time effects.

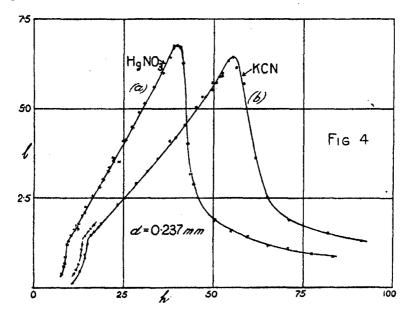
A satisfactory solution giving a low value for  $\sigma$  is easily found by using HgNO<sub>3</sub>; but it is difficult to find a correspondingly satisfactory solution for which  $\sigma$  is high. From previous experience we knew that undesirable time effects, which are generally present (when solutions other than those of mercury salts are employed), might be relatively small if we used n/4 KCN.\* We knew, however, that, in general, there would be a time effect, in solutions

<sup>\*</sup> Smith and Moss, 'Phil. Mag.,' April, 1908, p. 484.

of KCN, tending to make the surface tension decrease as the time of contact lengthened.

13. Difficulties due to Vuriability of Surface Tension.—When solutions of HgNO<sub>3</sub>, for which the time effect is known to be very small, are employed, the second branch BC of the *lh* curvé (cf. fig. 1) is very nearly linear. Hence, it is presumable that the surface tension between any other solution and mercury is not constant if the corresponding branch of its *lh* curve does not exhibit the same peculiarity.





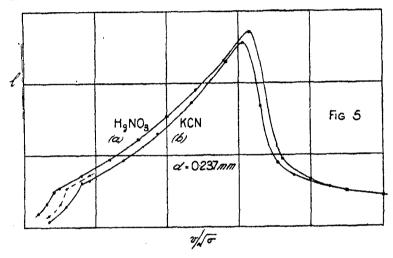
As will be seen, the second branch of the HgNO<sub>3</sub> curve is very nearly linear, while that of the KCN curve bends upwards as h rises. This difference suggests that the surface tension between the Hg and the KCN was not constant, as it might have been if we had hit upon the right concentration. By comparison with fig. 2, we see that (as was to be expected if it varied) the surface tension probably decreased as the time of contact lengthened.

14. Verification of the Preliminary Inference of §7.—The ratio of the surface tensions of the two solutions was measured by the capillary tube method and hence corresponded with comparatively long times of contact between the mercury and the solutions.

At the second critical points of the lv curves the times of contact are relatively long. We should therefore expect to get a more favourable test of the relation  $v_1/v_2 = \sqrt{(\sigma_1/\sigma_2)}$  from the observations at these points than

from those at the lower critical points, where the times of contact are shorter.

The observed value of  $\sigma_1/\sigma_2$  was 1.57; whence, if the suggested relation were true, we should have  $v_1/v_2 = 1.25$ . In fig. 5 the  $l\sigma$  curve for the HgNO<sub>3</sub> is repeated from fig. 3, but that for the KCN has been obtained by leaving the ordinates unchanged and reducing all the abscisse in the ratio 1.25:1.



It will be seen that the relation  $v_1/v_2 = \sqrt{(\sigma_1/\sigma_2)}$  holds, within the limits of experimental error, between the upper critical velocities.

Comparing the lower critical velocities, however, we see that  $v_1/v_2$  is greater than 1.25. This is what we should expect if, as is likely,  $\sigma_1/\sigma_2$  here exceeds 1.57.

A repetition of the KCN measurements at the lower velocities with a solution which had stood for some time in contact with mercury gave the dotted curve shown in the figure. It is probable that in this case the surface tensions differed less from those at the higher velocities and, as is seen, the curve agrees more nearly with that for the HgNO<sub>3</sub> than the corresponding part of the KCN curve obtained earlier.

The observations therefore support the view that, for both upper and lower critical velocities, the relation  $v_1/v_2 = \sqrt{(\sigma_1/\sigma_2)}$  is true.

But they do more than this. They suggest, if they do not fully prove, that if the surface tension had been constant throughout the measurements, in each case, the curves obtained by plotting l against  $v/\sqrt{\sigma}$  would have been identical. It is therefore worth while to attempt an interpretation of this possibility.

15. A Simple Relation Suggested by the Results of § 14.—The relation between the variables, as given by Lord Rayleigh's theory, can be written in the form

$$l/d = v \cdot 1/y \cdot \log a_0/a \cdot \sqrt{(\rho d/\sigma)}$$
.

Then, denoting the variables for two different solutions by the suffixes 1 and 2, respectively, we have

$$\frac{l_1}{d_1} = v_1 \left[ \frac{1}{y} \log \frac{a_0}{a} \right]_1 \cdot \sqrt{\frac{\rho_1 d_1}{\sigma_1}}$$

and

$$\frac{l_2}{d_2} = v_2 \left[ \frac{1}{y} \log \frac{n_0}{a} \right]_2 \cdot \sqrt{\frac{\rho_2 d_2}{\sigma_2}}$$

and if, as the results in § 14 suggest, we have always

$$l_1/d_1 = l_2/d_2$$
, when  $v_1 \sqrt{(\rho_1 d_1/\sigma_1)} = v_2 \sqrt{(\rho_2 d_2/\sigma_2)}$ ,

it follows at the same time that

$$\left[\frac{1}{y}, \log \frac{a_0}{a}\right]_1 = \left[\frac{1}{y}, \log \frac{a_0}{a}\right]_2.$$

From which, if y can be considered constant, we get the simple result that the initial disturbance is the same fraction of the disintegrating disturbance when the velocities  $v_1$  and  $v_2$  are in the ratio  $\sqrt{(\sigma_1/\rho_1 d_1)}$ :  $\sqrt{(\sigma_2/\rho_2 d_2)}$ .

16. More Accurate Determination of the Relation between the Form of the le Curve and the Diameter of the Jet. Verification of the Relation of § 15.— The immediate object of the experiments (a) and (c) was to test whether the critical velocities are connected by the relation  $v_1/v_2 = \sqrt{(d_2/d_1)}$ , when  $\sigma$  is constant.

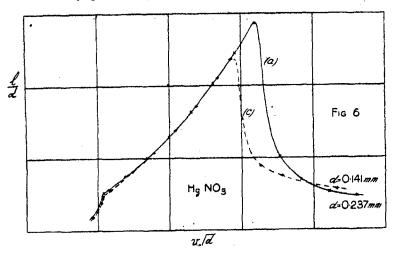
For this purpose it would have been sufficient to re-draw the curves (a) and (c) of fig. 3, keeping the ordinates the same but multiplying each abscissa by  $\sqrt{d_1}$  in the one case and by  $\sqrt{d_2}$  in the other. We made this change in the abscisse, but, instead of keeping the ordinates the same as in fig. 3, we divided each by the diameter of the jet. We could then, in addition, see at a glance whether § 15 was confirmed.

The result is shown in fig. 6, where, therefore, the ordinates represent the values of l/d and the abscisse those of  $v\sqrt{d}$ , for the two jets.

The curves are even more nearly alike than those of fig. 5. It is only in the region of the upper critical velocities that they differ appreciably.

In estimating how much importance to attach to this difference, it must be remembered that small uncontrollable differences in the experimental conditions are always present. It is impossible, for example, to construct a pair of nozzles identical in all respects except size. Small differences in shape, e.g. in the cylindricality of the orifice, influence the properties of the jet perceptibly and we think, from experience, that the differences shown

in fig. 6 are more than probably due to causes of this nature. Moreover, the results already given in § 6, for a series of jets, are evidence that, for



the upper critical velocity, the result  $v_c \propto 1/\sqrt{d}$  is, in general, not far from true.

17. Summary of Section I.—We have performed a few supplementary experiments with jets of mercury and of other liquids falling in air, but before proceeding to them it will be convenient to summarize the results already obtained.

These results apply only to mercury jets of different diameters and surface tensions falling into aqueous solutions. The density (and viscosity) of the jet-fluid has remained unchanged.

(i) We have found that there are two critical velocities and that, for any pair of jets, corresponding critical velocities are connected by the relation

$$v_1: v_2 = \sqrt{(\sigma_1/d_1)}: \sqrt{(\sigma_2/d_2)}.$$

- (ii) We have taken the view that the critical velocities have their origin in certain known peculiarities of fluid motion which, we suppose, cause comparatively sudden changes, at particular velocities, in the initial amplitude of the disturbance under which the jet breaks down.
- (iii) We have then found that the ratio of the initial to the final (disintegrating) disturbance is the same, at corresponding critical points, for all the jets examined.
- (iv) The changes occurring at such critical points are thus always of exactly the same nature. Change of diameter or of surface tension merely alters the velocity of efflux at which each change occurs.

(v) We have found further that these regularities are not confined to the critical points. The sequence of changes of initial amplitude between these points is again always the same.

In consequence, the results can be correlated in the following simple way:-

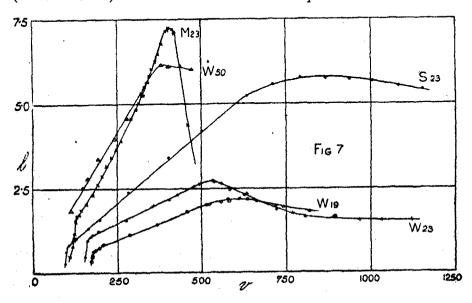
(vi) For any pair of jets, the initial disturbance is the same fraction of the final disturbance for any pair of velocities whose ratio is  $\sqrt{(\sigma_1/d_1)}$ :  $\sqrt{(\sigma_2/d_2)}$ , and, with these velocities, the jet-lengths are in the ratio

$$l_1: l_2 = d_1: d_2$$

Section II.—A Comparison with Jets of other Liquids.

18. Critical Velocities for Jets of Different Liquids formed in Air.— Examination of the properties of jets of different liquids falling through air should afford an opportunity of testing our previous inference with respect to the influence of density. A comparison of mercury jets with water jets suggested itself not only because the densities of the two liquids are very different, but also because of Savart's results for water jets of comparatively large diameter, produced in a different way.

The time at our disposal did not permit many experiments. Fig. 7 shows one *lv* curve for mercury (M 23) and two (W 23 and W 19) for water. It also contains one *lv* curve for methylated spirit (S 23). The narrower nozzle (diam. 0.019 cm.) was used for the water only. The wider nozzle (diam. 0.023 cm.) was used for each of the three liquids.



The figure contains also an incomplete series of observations for water (W 50), with a nozzle of which the diameter was 0.0504 cm.

If the expression in § 8 is general, corresponding velocities should be in the ratio of the values of  $\sqrt{(\sigma/\rho d)}$  for the different jets.

We took Quincke's values\* of  $\sigma$  for the water and mercury. The values of  $\sigma$  and  $\rho$  for the methylated spirit were found by direct comparison with the water used.

The critical velocities  $v_1$  and  $v_2$ , in the cases in which they were determined, are given in round numbers (from fig. 7) in the Table which follows:—

	d.	v <sub>1</sub> .	r <sub>2</sub> ,	$v_1/\sqrt{(\sigma/\rho d)}$ .	$v_2/\sim'(\sigma/\rho d)$ .
Water σ = 74 ρ = 1	cm. 0 <b>·02825</b> 0 <b>·0186</b>	om./sec. 160 180	em./sec. 525 600	2 ·84 2 ·85	9·8 9·5
Mercury σ = 847 ρ = 18.55	0 02325	125	405	8.0	9.7
Methylated spirit $\sigma = 24.4$ $\rho = 0.82$	0 .02825	100	(800)	2 .80	(22 ·4)

It will be seen from the numbers in the final columns that

$$v_c \propto (\sigma/\rho d)^{\frac{1}{2}}$$

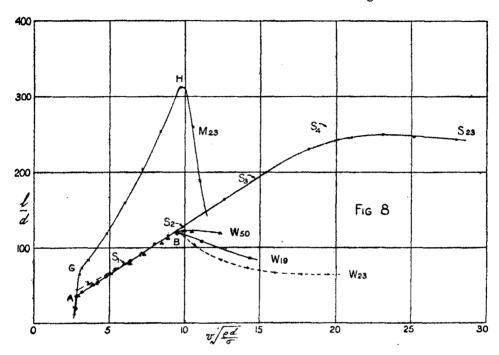
is not far from true for the liquids water and mercury, and also for methylated spirit when the lower critical velocity is considered. In the latter case, however, the upper critical velocity is far too high. Instead of being in the neighbourhood of 350 cm. per second, as it should be to agree with the results for the other liquids, its value is about 800 cm. per second. We have not investigated this discrepancy sufficiently to be able to express a final opinion as to its cause. We found, however, that the viscosity of the methylated spirit was 43 per cent. greater than that of the water. In contrast with this, the viscosities of water and mercury are nearly equal. Further experiment would, no doubt, define the extent to which the critical velocity is affected by the viscosity of the liquid (cf. § 8).

19. Analysis of Water Jet Results.—It was now of interest to compare the curves of fig. 7 by the method of § 16.

In order to examine the relation between the water curves, it would have sufficed to plot the values of l/d against those of  $v\sqrt{d}$ ; but, to permit a

<sup>\* &#</sup>x27;Ann. d. Phys.,' vol. 52, p. 1 (1894).

wider comparison, we have plotted the values of l/d against those of  $v\sqrt{(\rho d/\sigma)}$  for each case of § 18. The result is shown in fig. 8.



It will be seen that the water curves, instead of being widely separated as in fig. 7, are now practically coincident in the region (marked AB) between the critical points. The agreement between the  $W_{19}$  points (marked by  $\odot$ ) and the  $W_{50}$  points (marked by  $\triangle$ ) is very close. They lie, very nearly, upon a straight line passing through the origin. Except at the lower values of v, where the agreement is not very good,\* the  $W_{29}$  points (marked by +) lie on the same straight line as the others.

Thus the relation outlined in § 15 appears again to hold; but, between the two critical points, it can now be expressed even more simply than before.

This happens because, if we assume that the portions of the curves lying between the two critical points are on a straight line passing through the origin and if, as in § 15, we have

$$l/d = v \cdot 1/y \cdot \log a_0/a \cdot \sqrt{(\rho d/\sigma)}$$

\* It should be mentioned that, under the experimental conditions, the length of a water jet is less easy to fix than that of a mercury jet. The end of the jet is more clearly visible in the latter case than in the former. The wetting of the glass by the water also causes trouble at the lower velocities.

it follows that the quantity

$$\frac{1}{y}\log\frac{a_0}{a} = \frac{l}{d} / v \sqrt{\frac{\rho d}{\sigma}} = \tan\theta,$$

where  $\theta$  is the slope of the line AB, is constant for all the jets.

The simplest interpretation of this is (y constant) that  $a_0/a$  is constant and that therefore the initial amplitude of the disintegrating disturbance is the same fraction of the final disturbance, for all the jets, for all velocities lying between the limits specified.

Fig. 8 shows also another interesting result. The methylated spirit points (marked by ·) lie almost exactly on the same line (AB) as the water points. The initial amplitude is thus not only a constant fraction of the final amplitude as with water; but, in addition, this fraction has the same value for both liquids.

Without making a quantitative comparison it can be seen at once, from fig. 8, that, besides being variable, the initial amplitudes are much smaller fractions of the final amplitude when mercury is used.

These differences between mercury and the other liquids must of course have a cause. Possibly they are connected with the fact that mercury does not wet glass. It may be, also, that the magnitude of the initial disturbance is influenced by pulsations of pressure, occurring within the jet as each drop forms and breaks away, whose effects (owing, for example, to differences of density) are not of the same relative importance in each case.

In some approximate experiments with orifices of the kind referred to below (§ 22) we found that, although the jet-lengths for mercury were (as above) longer than the corresponding ones for water, the *lv* curves for the former liquid were now, as nearly as we could decide, parts of straight lines passing through the origin. With such orifices it therefore appears that, as with other liquids, the initial amplitude for mercury is now a constant fraction of the final amplitude.

20. Numerical Comparisons between Water Jets and Mercury Jets.—If we assume the value of y to be that calculable from Lord Rayleigh's theory, viz.,

$$y = \sqrt{8 \times 0.343} = 0.97,$$

we can compare the initial amplitudes quantitatively.

Thus, from the water curves, we get very nearly  $l/d + v \checkmark (\rho d/\sigma) = 13$ , and hence  $a_0/a = e^{12.6}$ . Similarly, from the mercury curve, we get at G (the lower critical velocity)  $a_0/a = e^{22.8}$  and at H (the higher critical velocity)  $a_0/a = e^{31.7}$ . Whence we get that the initial amplitude between A and B (water and methylated spirit) is, in round numbers, 20,000 times as great as that at G (mercury), while that at G is about 8,000 times as great as that at H.

21. Confirmation of Lord Rayleigh's Theory of Jets.—Lord Rayleigh has pointed out that some of Savart's results can be explained on the assumption that "the disturbances remain always of the same character, so that the time of disintegration is constant."

This suggestion with respect to Savart's jets, that the time of disintegration is constant, is clearly true for our water jets between A and B (fig. 8). We have measured both l and v (fig. 7) and have found that the ratio l/v=t is constant.

Another consequence of the above assumption, pointed out by Lord Rayleigh, but apparently at variance with Savart's results, is that the jet. length for a given velocity of efflux should be proportional to  $d^{3/2}$ . This inference is, however, again in agreement with our results. For example, when the velocity is 500 cm./sec., it will be seen from fig. 7 that the jet-lengths are in the ratio 1.38:1, while  $(d_1/d_2)^{3/2}=1.40$ .

If the data upon which Savart bases his conclusion (that the jet-length is proportional to the diameter) be examined, it will be found that the evidence for the conclusion is very slight. It is contained in two series of results; for orifices of which the diameters were 3 and 6 mm. respectively.

Savart himself remarks that the difficulty of obtaining definite measurements increases with the diameter of the jet. The jet-length becomes increasingly dependent upon extraneous disturbances until, as he points out, it is impossible to obtain even approximate measurements when the diameter of the orifice is 9 mm. Even with the narrower jets used by him, these effects are considerable and it will be found that only one of his sets of results for the 6 mm. orifice agrees reasonably with his first "law"—that the jet-length is proportional to the velocity of the efflux. While, when all his results with this orifice are considered, they furnish as little support for his second "law" as for that which we have found to be true for the jets we have used.

It is interesting to compare Savart's results with his narrower jet (diameter 0.3 cm.), which were comparatively regular, with our data.

For this purpose we may take his "fourth series," in which the jet was protected as far as possible from outside disturbances. If, for this set, l/d is plotted against  $v\sqrt{(\rho d/\sigma)}$  we get a straight line passing through the origin which, curiously enough, coincides almost exactly with the line AB. This relationship is shown in fig. 8, where the heads of the arrows marked

<sup>\* &#</sup>x27;Theory of Sound,' vol. 2, p. 363 (1896).

<sup>+</sup> I.e., for different velocities of efflux.

<sup>† &#</sup>x27;Ann. Chim. Phys.,' vol. 53, p. 368.

<sup>§</sup> Loc. cit., p. 368.

 $S_1$ ,  $S_2$ ,  $S_3$ ,  $S_4$ , represent Savart's results treated in this way. It should be remarked, however, that in this case d, the diameter of the orifice, is not, even approximately,\* the mean diameter of the jet. For equal velocities, this jet was more than 60 times as long as the narrowest jet we used and more than 15 times as long as the widest.

Lord Rayleigh, referring to the discrepancy between Savart's results and theory, remarks that "it may well be doubted whether the length of the continuous portion obeys any very simple laws, even when external disturbances are avoided as far as possible." We have therefore thought it of interest to point out that conditions can be found under which the discrepancy between theory and experiment disappears.

22. Dependence of the Critical Velocities upon the Shape of the Nozzle.—
There is one respect in which Savart's results differ very noticeably from ours. They show no evidence of critical velocities. The jet-length continues to increase long after the velocity reaches the value above which, if his jets had behaved like ours, a shortening would have ensued.

It is easy to show experimentally that this difference is due to the difference between the orifices. We made an approximate series of observations with an orifice of about 0.025 cm. diameter, similar in character to those used by Savart. It was constructed by boring a hole, bevelled from the outside, in a thin steel plate. This plate was fixed horizontally, at the end of the supply tube, in the position previously occupied in turn by each of the glass nozzles already described. We found for water with this orifice that, as in Savart's experiments, the jet-length continued to increase until we reached the greatest head we could apply conveniently. The velocity of efflux was then more than three times as great as that which, with a glass nozzle of the same diameter, would have been the upper critical velocity.

23. The Origin of the Critical Velocities.—The results just described throw light upon the cause of the phenomena we have observed. They show that the conditious of escape of the fluid may be such that the upper critical velocity either does not exist or is relatively very high and therefore invite a comparison between one kind of orifice and the other. This comparison can be made, very roughly, as follows:—

When the liquid leaves the orifice of a nozzle such as we have used, assuming that "turbulence" has not arisen within the tube, the stream-lines will be practically parallel. Owing to viscosity, however, the velocity will be greater at the centre of the jet than it is near the sides. This difference of velocities will not be maintained after the liquid leaves the orifice, for the

force exerted upon the moving liquid by the walls of the nozzle will disappear from each element of the jet as it forms. But viscous forces will continue to operate between the more rapidly moving central part of the element and the less rapidly moving outer parts until the differences between their velocities are destroyed.

Since the velocity along the axis, neglecting the effects of gravity, must thus tend to fall after the liquid leaves the nozzle, the axial stream-lines must tend to broaden and, while this is occurring, the velocity along these stream-lines will have a radial component from the centre outwards. It is while the liquid particles are executing the movements necessary at this stage of the jet's existence that stream-line motion seems most likely to break down. We may suppose, in fact, that excessive radial velocity is a precursor of turbulence and may expect the appearance of the latter to be controlled by the means at disposal for the conversion of radial kinetic energy into other forms. To express this view in another way, imagine an element of the jet of length dl to have its radius increased from r to r+drby the influx at its centre of a volume dV of liquid possessing kinetic energy, of which the amount  $\alpha \rho v^2 dV$  may be regarded as radial and tending to degenerate into energy of turbulence. The relation between dV and dris dV = dl.  $2\pi r dr$ ; that between dr and dS, the increase in the surface of the element, is  $dS = dl \cdot 2\pi dr$ . Hence the increase of surface energy corresponding with the influx of dV is  $\sigma dS = \sigma dV/r$ . And if  $\sigma dV/r$ exceeds  $\alpha \rho v^2 dV$ , i.e., if  $\sigma/\rho r$  exceeds  $\alpha v^2$ , the increase of surface energy would be more than sufficient to replace the whole of the radial kinetic energy from which turbulence might arise and so could prevent the degeneration of energy which otherwise might ensue.

Such considerations indicate, perhaps more clearly than those of § 8, why it is that, with our nozzles, there are critical velocities which depend upon the relative values of  $\sigma/\rho r$  and of  $v^2$ .

In the case of an orifice like that used by Savart, the region within which there are appreciable differences of velocity, between contiguous moving elements of the fluid, is of restricted extent and the effects of viscosity are reduced to a minimum. In this case the stream-lines converge as the liquid leaves the orifice. The velocity is greatest at the sides; but the pressure is greatest at the centre. The hydrodynamic forces operate to remove both these differences, and at a short distance below the orifice (gravity neglected) the stream-lines become parallel, and the velocity becomes uniform, across the jet. The cause of turbulence present in the first case has disappeared.

24. Summary of Section II.—The experiments of §§ 18 to 23 may be

described as forming a link between the experiments of §§ 1 to 16 and the well-known experiments of Savart.

Nozzles of the same kind as before were used, but the jet liquid was now surrounded by air. Using mercury and water, the relation  $v_c \propto (\sigma/\rho d)^2$  was tested and found to be nearly true.

The mercury jet had similar properties to those previously studied. As before, between the critical velocities, dl/dv increases as v increases.

Water behaves differently. Jets of diameters between 0.18 and 0.5 mm. were examined. Their properties may be formulated thus:

(i) Between the critical points, each lv curve forms part of a straight line passing through the origin. Hence for each jet

$$dl/dv = l/v = t = a$$
 constant,

where t is the time of disintegration, i.e., the time taken by each element of the liquid to pass from the top to the bottom of the jet.

- (ii) The value of this constant increases with the diameter of the jet, but when l/d is plotted against  $v\sqrt{(\rho d/\sigma)}$  the observations for all the jets fall upon the same straight line.
  - (iii) From this it follows that

$$l/d + v\sqrt{(\rho d/\sigma)} = l/v \cdot \sqrt{(\sigma/\rho d^3)} = t\sqrt{(\sigma/\rho d^3)}$$

has the same value for all the jets.

- (iv) The cause of disintegration is taken to be the disturbance which originates at the orifice.
- (v) Lord Rayleigh's theory leads to the result that the rate of growth of this disturbance is given by

where a is the initial amplitude, k is a constant (§ 9),  $\tau$  is the time which has elapsed since the disturbance began.

(vi) If this theory is applicable, the ratio of the initial to the final amplitude for each jet is given by

and is therefore the same for all, since we have found  $t\sqrt{\sigma/\rho d^3}$  to be constant. The initial amplitude is, apparently, a constant fraction of the diameter of the jet.

- (vii) As Lord Rayleigh has pointed out, some of Savart's results suggest a simple relation of this kind, while others suggest that the relation is more complicated.
  - (viii) The present experiments indicate that if narrower jets had been

used by Savart, the simple relation would have sufficed to define their behaviour.

(ix) The critical velocities, if they exist, obey a different law when, as in Savart's experiments, the liquid escapes through a sharp-edged hole in a horizontal plate. Our critical velocities owe their existence to the shape of the nozzle we have used. This favours turbulence—eddies or vortices—as indicated in the text.

On Residual Magnetism in Relation to Magnetic Shielding.\*

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(Communicated by Prof. J. A. Fleming, F.R.S. Received February 17, 1917.)

The present communication records the final stages of an investigation, of a somewhat exhaustive character, into the various problems which were presented by the necessity for constructing a magnetic shield suitable for large spaces, and capable of giving such a degree of shielding that the internal field caused by the earth should not exceed the order of magnitude  $10^{-3}$  C.G.S. unit. The theoretical calculation of the best form of shield, and the details of its construction, were given, together with an examination of the various methods of testing the efficiencies of large shields, in the first paper.† A study of the effect of leakage through small air spaces was made at the same time, and it became apparent that not only this problem, but several others which are vital to the production of the theoretical efficiency of a shield, needed a more careful study than they had received hitherto.

The usual process adopted for removing permanent magnetism from a shell or set of shells, by the reversals of a slowly decreasing current, ceases to be efficient when the magnetisation is very small, unless special methods are introduced, and there was previously no definite indication of the degree of accuracy with which the magnetic induction at any point due to a coil, wound in a helix on one member of a set of spherical shells, could be either predicted or measured. A study of these problems was made, and the results described in a second paper.‡

<sup>\*</sup> This investigation has again been facilitated by a grant made by the Council of the Society out of the Gore Fund.

<sup>† &#</sup>x27;Boy. Soc. Proc.,' A, vol. 92, p. 529 (1916).

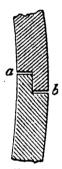
<sup>† &#</sup>x27;Boy. Soc. Proc.,' A, vol. 93, p. 129 (1917).

It is now possible to correct the theoretical formulæ for the effect of the angle of the helix in a loose winding under these circumstances, and, by a method which adopts an exploring coil with only one turn, to measure accurately very small values of the magnetic induction, to an order as low as 0.7 C.G.S. unit, in any one of a set of spherical shells surrounded by one or more magnetising coils, with results in close accord with theoretical calculation. The ordinary process of demagnetisation of an iron shell is in this respect now on a definite—and, in fact, delicate—quantitative basis. In the same paper, moreover, it was shown that the delay in reversal of magnetic induction, caused by eddy currents, is effectively negligible when the magnetic induction is not greater than about 300 C.G.S. units. This fact removes what would otherwise be a source of considerable difficulty in the production of an effective shield, for a shield constructed according to the necessary theoretical specification, for large spaces, outlined in the first paper, is so constituted, as regards the thicknesses of individual shells and the distances between them, that currents which would ordinarily be used in removing permanent magnetism do not produce, in any individual shell, magnetic inductions which greatly exceed this value.

There is, however, one outstanding problem whose solution is necessary to complete the study of magnetic shielding on its experimental side. necessity for a determination of what constitutes "effective demagnetisation" was pointed out in the second paper. In other words, there is a limit beyond which the permanent magnetism of a set of spherical shells cannot be removed by the use of magnetising coils in which currents are reversed and diminished. A study of this limit is one of the main objects of the work described in the present communication, which has shown that there is a phenomenon, of fundamental importance in the magnetic behaviour of iron, which has probably escaped attention on account of the previous restriction of accurate quantitative work on iron in large masses to the cases in which the magnetic induction is large. For one of the main conclusions of the present paper is that the permanent magnetism of a mass of iron can only be removed by the reversal and diminution of a current when all steady fields. of which that of the earth is a particular example, are absent. Although the field of the earth is small, it is, nevertheless, very large in comparison with the limiting field which is desired in the interior of the magnetic shield, and the succeeding experiments show that, when it is not approximately neutralised by a current flowing in a coil just outside the shield, the reversals of current in any other coil on an inner shell are, in certain cases, capable of producing a stronger degree of polarisation than they were actually designed to remove. The whole shield must, in fact, be surrounded,

during the process of demagnetisation, by a current which will reduce the field just outside the shield as nearly as possible to zero.

The details of the apparatus have been described sufficiently in the previous papers. We may at this point merely recall that the shield consists of four concentric spherical shells, numbered 1, 2, 3, 4, from innermost to outermost, and wound with magnetising coils, to which the same numbers relate. Although each shell was originally a pair of hemispheres in contact, the junction planes have now been machined so that each half of any one shell penetrates the other half, the method being shown in fig. 1. Except in the case of the second shell, there is a small



Number of shell	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	A SAME			
	Units	Units	Units	Units	Units
1				~045	-0.06
2				- I·38	-0.17
3	+1	-2	- 6.38	-4:14	-0.42
4			+4.71	+5.52	-1.26

Fig. 1

F1G. 2.

remaining air space of the form indicated in the figure, but in other respects the closeness of fit is quite satisfactory. It is, in fact, the closeness of fit which prevents complete contact at the points a, b, and it will be noticed that there is no continuous air space extending through the material of the shell at any point.

The junction planes of the shells are all placed at right angles to the direction of the earth's field, and the magnetising coils are normal to the diameter in the direction of this field. The axis of the inductor ring inside the shells is at right angles to the magnetic meridian, and coincides with a diameter in the planes of junction. These adjustments are identical with those made in the previous experiments, and the work has again been carried on in the Siemens Laboratory at King's College.

Throughout this communication, forces are called positive when they have the same sign as that of the earth, and positive forces are plotted above the axis of the abscisse in all the diagrams. The subsequent curves show directly the relation between the average magnetic intensity in the hollow of the shield and the angular position of the inductor ring. The plane of the latter is vertical when the angle is 0°, and horizontal when it is 90°. The

direction of the earth's magnetic field corresponds to an angle 67° on the scale of abscissæ. Further details may be found in earlier papers.\*

Preliminary experiments with the smallest shell showed that the machining had greatly improved its efficiency as a shield, by the considerable reduction in magnetic leakage. In the original experiments of the first paper, before the shell was machined, the field inside it was 0.116 C.G.S. This is now reduced to 0.06 C.G.S. unit without the use of appreciable demagnetisation of its material, and the curve obtained by rotating the inductor ring within it is much more nearly a sine function of angle; this is an indication of diminished leakage and of uniformity in the internal Experiments with groups of two and of three shells indicated a similar degree of improvement, but the details of this work are not given, for the main object in view was the investigation of the ultimate shielding ratio which can be attained in practice with the four complete shells arranged with a common centre, and all the characteristic features of the curves obtained with a selection from the shells are reproduced in the experiments involving four shells, in which, on account of the small forces then concerned, measurements of a much greater delicacy can be made, and disturbing factors are of greater relative importance.

## Experiments with Four Complete Shells.

Before proceeding to an account of these experiments, it is convenient to collect together, for reference, certain data which were calculated in the last paper,† together with some further results of calculation found by the same method, which can be verified readily by the reader. They relate, of course, only to the particular set of shells used throughout these experiments, but in their general scope they give valuable information in connection with any magnetic shield built up according to a specification of maximum efficiency. In the estimation of the maximum value of the magnetic induction for various combinations produced by a definite current, it is convenient to take a single shell wound with a coil carrying that current as a unit. is done in the diagram (fig. 2), where the third shell alone is the unit. The magnetising coil used in any other case is indicated in the figure by a set of small circles. The large circles represent the shells forming part of any configuration. The coil on the third shell as unit was wound on the inner surface.

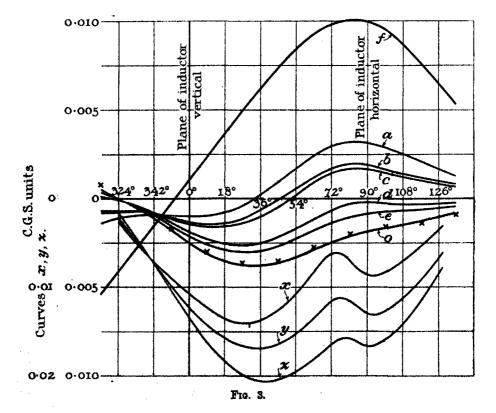
With this figure may be combined the statement that a current of C ampères in the magnetising coil produces a maximum magnetic induction

<sup>\* &#</sup>x27;Roy. Soc. Proc.,' A, vol. 92, p. 529 (1916).

<sup>† &#</sup>x27;Roy. Soc. Proc.,' A, vol. 93, p. 129 (1917).

of 5.9 C.G.S. units in the single shell taken as standard. The figure is therefore such that 1 unit = 5.9 C units of magnetic induction. This value, which relates to small currents, must be increased for larger ones owing to the influence of the curve of magnetisation.

The experiments described in the preceding paper left the shells in a polarised condition as the result of the last applied current of 5.5 ampères in the third magnetising coil. This current gives rise to maximum magnetic induction of amounts  $B_{\text{max}} = -20$ , -68, -204, +272 C.G.S. units in the shells numbered 1, 2, 3, 4 respectively, where the first value is approximate. From this starting point, the first new experiments made consisted of the connection of the magnetising coils 1, 2, 3 in series, in order to give alternating signs to their effects on any particular shell—this question of sign was considered in the second paper—and the passage of a current of 4.7 ampères through them initially. This current was gradually reduced by stages to 0.01 ampère. Ten reversals were made during each stage, the time interval between each reversal being four seconds, and the number of such stages or steps in the reduction was 40. The full line curve o in fig. 3 exhibits



the result, and it demonstrates the final existence of a field of 0.0038 C.G.S. unit opposed to that of the earth, in the space internal to the four shells.

It is desirable at once to place emphasis on this important experimental result, for it has been obtained consistently throughout the work with these spherical shells. As an illustration, we may refer back to the first paper,\* in which, the shells being then in their initial state before machining, the same character was obtained in the results. For the treatment to which they were subjected, prior to the determination of the curves in fig. 3 of that paper, was demagnetisation by the use of coils 1, 2, 3, in this order, but separately, the initial maximum currents being 7, 8, 7.5 ampères respectively. The curves x, y, z in fig. 3 of the present paper were then obtained by rotation of the inductor, and will be referred to again in connection with later experiments which bear out the same conclusion.

It might be thought that the poles or intersections of any shell with the diameter which is axial to all the turns of a magnetising coil are connected For, in their neighbourhood, the magnetic induction with this effect. produced by a current in the magnetising coil is notably smaller, and effective demagnetisation of a shell in these regions would be difficult. In order to test this point, another coil was wound on the third shell at right angles to the coil already present, and embracing an angle of about 10° on either side of the axis of this coil, thus covering an appreciable zone of the shell at the poles. It had six turns, and its axis, normal to its plane of winding, coincided with the axis of the inductor. A current of 6.8 ampères was passed through this new coil and gradually reduced during reversal by steps to the value 1/13000 ampère. The only effect produced was a slight change of phase of the curve o, fig. 3, with no change in amplitude Demagnetisation by the use of coils 1, 2, 3 from the previous terminal value of 0.01 ampère to 0.00006 ampère was then carried out without producing any effect, on the internal field in the shell, which could be measured. It is therefore evident that we are in the presence of a phenomenon which does not arise from the poles of the coils. Up to this point no current had been applied to the fourth or outermost coil in the present experiments.

The internal force of 0.0038 C.G.S. unit, which was now present, could not, from its sign, represent a partially shielded field of the earth, but necessarily had its origin in some disturbing factor which could only be regarded as residual magnetisation incapable of removal by reversed and diminished currents of moderate amounts in the three inner magnetising coils. As a preliminary experiment, designed to elucidate the nature of the effect, a current of 0.457 ampère was passed through the fourth or outermost

<sup>\* &#</sup>x27;Roy. Soc. Proc.,' A. vol. 92, p. 529 (1916).

coil in such a direction as to oppose the earth's field in the interior of the coil, and maintained constant. During the passage of this steady current, the process of demagnetisation was carried out in the usual manner by passing a current of 4.7 ampères through coils 1, 2, 3 arranged in series, and reducing it by steps, with many reversals, to 1/13000 ampère. The circuit in the fourth coil was then broken, and curve a, fig. 3, taken during rotation of the inductor. This curve indicates a positive maximum force, of the same sign as the earth's field, in the interior of the shield. The actual value of this force is +0.00324 C.G.S. unit. It is evident that this will include an effect due to permanent polarisation mainly of the fourth shell, round which a steady current was maintained.

This current of 0.457 ampère round the fourth shell was then restored. and gradually reduced by steps during reversal to 1/6000 ampère. Curve b, fig. 3, was then obtained by the examination of the internal space. The maximum force in the space, as read from curve b, is +0.00193 C.G.S. unit, notably smaller, but again of the same sign as the earth's field. The shells have apparently at this stage been demagnetised very completely throughout the whole of their mass, but in order to ensure complete treatment, currents of 0.01, 0.109, 0.555 ampère were passed successively through coils 1, 2, 3 in series, and reduced in each case by small steps with many reversals to 1/6000 ampère, so that all the shells should now be demagnetised down to The use of the current 0.01 ampère produced no difference capable of detection in the internal force. The currents 0:109 and 0:555 produced some differences, and the results of their application are shown in curves c and d respectively. Demagnetisation with the large current, 0.555 ampère, was repeated, but it only led to a very slight reduction in the force shown by curve d. A larger initial current of 105 ampère was then used in place of 0.555 ampère, and the process repeated. Curve e shows the result. Finally, the same process was carried out with an initial current of 2.5 ampères, and the original curve o was restored, the observations made during the rotation of the inductor in this experiment being indicated in the figure by crosses on the original curve o.

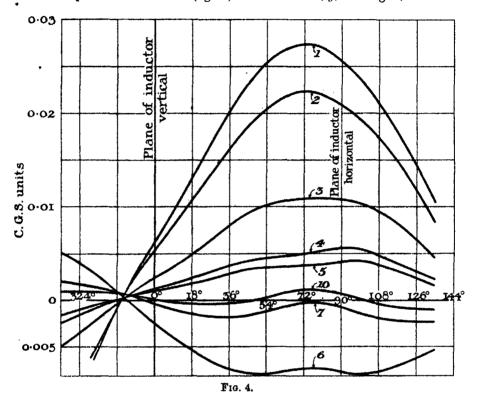
In this manner, it was therefore found possible to remove the negative force of 0.0038 C.G.S. unit by the actual establishment of residual magnetism, and subsequently to restore it again by demagnetisation. At the same time a considerable degree of control was established over the value of the internal force within the shield. It will be noticed that the minimum field obtained up to this point is given by curve c, and has the value 0.00175 C.G.S. unit approximately in the direction of the earth's field, and with it is a negative field of 0.0016 unit associated primarily with leakage.

This result, which is the best obtained hitherto from the point of view of close shielding, can, however, be improved. The essential feature to which attention should be drawn is the use of the original steady current of 0.457 ampère in the outermost coil. For this constituted the only difference in procedure adopted in this set of experiments when compared with those made previously, and the more satisfactory results obtained must in some manner be due to it. This conclusion is enhanced by the fact of the restoration of the original curve o when a demagnetisation of the shells was carried out, without the presence of this steady current in the fourth coil, with a current exceeding 2 ampères initially.

In order to illustrate and examine this process further, a larger current of 0.893 ampère was then passed through the fourth coil and maintained constant during the demagnetisation of the shells from an initial current of 5 ampères in coils 1, 2, 3 arranged in series; the current of 0.893 being finally reduced by steps during reversal to 1/6000 ampère. Curve f was then obtained for the internal space, and has a maximum ordinate of +0.0101 C.G.S unit, whereas the maximum ordinate prior to demagnetisation with the fourth coil had the slightly greater value +0.0122 unit.

Fig. 4 shows the effect of carrying this process to a further extent. A current as large as 2.5 ampères was passed through the fourth coil in such a direction as to oppose the earth's field in its interior, and maintained con-Meanwhile the shells were demagnetised by a current of initial value 9.2 ampères passed through the coils 1, 2, 3 in series, and reduced during reversals to 1/6000 ampère. After breaking the current in the fourth coil, curve 1, in fig. 4, was obtained as the representation of the inside field. Its maximum ordinate is +0.0275 C.G.S. unit, and on demagnetising subsequently with the fourth coil from 2.4 ampères downwards, this ordinate was reduced to +0.0224 unit, as shown on curve 2 of the same figure. The remaining processes employed in the experiments which led to fig. 3 were then carried out for fig. 4. Thus a series of demagnetisations was made with initial currents of ascending values 4.8, 7.5, 10.2, 12.5 ampères in coils 1, 2, 3, arranged in series as before, and the maximum ordinates corresponding to these operations were +0.0109, +0.0052, +0.0042, and -0.008 C.G.S. unit respectively, as shown on curves 3, 4, 5, 6 of fig. 4. As before, by the application of a sufficiently large demagnetising current (12.5 ampères), the positive force within the shield, given by curve 1, has been removed and a negative force obtained. It will be noticed that curve 6 has an ordinate of magnitude 0.0073 C.G.S. unit at 78° in a direction parallel but of opposite sign to the earth's field, and that the ordinates on either side at angles 51° and 102°, which are equidistant from the position, are -0.008 and -0.00795 unit respectively, that is to say, are effectively equal.

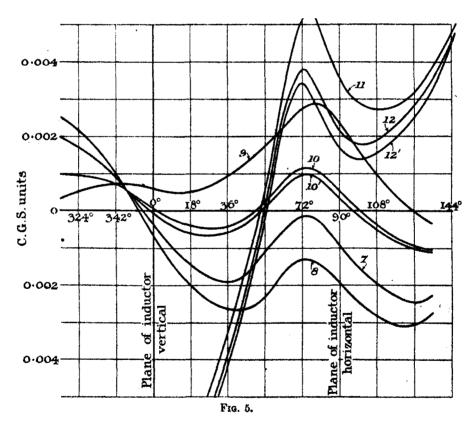
On comparison of curve 6 (fig. 4) with curves z, y, z in fig. 3, it will be



seen that they all have two points of inflexion, whereas curve o (fig. 3) has no such points. Experience with these shells has demonstrated the necessity for removal of every trace of polarisation, until the ultimate negative force in the shield gives this particular wave form when the inductor is rotated. If this wave form has once been obtained, it is possible to proceed to the highest degree of shielding. We have shown already that the best shielding result obtained with curve o (fig. 3) as a basis, involved a final internal force of +0.00175 C.G.S. unit, associated with a leakage field of 0.0016 unit, approximately. It was stated at the time that the results could be improved, and it is, in fact, shown later that a force as low as +0.00117 C.G.S. unit can be obtained. The importance of the points of inflexion is contained in the fact that their existence is a general indication of the approximate absence of polarisation, capable of removal by the magnetising coils, the wave form then denoting a mere superposition of the shielded

effect of the earth, which is a uniform field, giving a pure sine curve when the inductor is rotated, and the leakage field with a more restricted degree of symmetry. When these points of inflexion are once obtained, they persist in a remarkable manner in the subsequent curves derived by variation of the demagnetising currents in the four coils. For example, reference to the earlier paper will show that the curves 1 and 2 (fig. 3) of that paper,\* which were obtained after the curves x, y, z in fig. 3 of the present paper, maintain the same characteristic wave form.

In the further development of the work, the curves are plotted on a larger scale in fig. 5. A current of 0.675 ampère was now maintained constantly in the fourth coil in such a direction as to oppose the field of the



earth inside the coil. The process of demagnetisation of the shells was carried out simultaneously from an initial current of 19 ampères in the coils 1, 2, 3, arranged in series. The current in the fourth coil was then broken, and the interior of the shield explored by the inductor ring, with

<sup>\* &#</sup>x27;Roy. Soc. Proc.,' A, vol. 92, p. 546 (1916).

the result shown in curve 7 (fig. 5). The current in the fourth coil was then restored and reduced by steps during reversals. Curve 8 (fig. 5) was then taken, and it indicates a negative force directly opposed to the earth's field, of magnitude -0.0013 C.G.S. unit.

The current in the outer coil was then maintained at 0.751 ampère. and the shells demagnetised as before from 1.9 ampères. field obtained on breaking the outer current is shown in curve 9 (fig. 5). The subsequent demagnetisation by the fourth coil from 0.751 ampère changes the distribution into that indicated in curve 10 (fig. 5). This curve has ordinates at angles 315° and 135°, equal to one another, and of magnitude 0.001 C.G.S. unit, and the ordinate at 72°, coinciding with the direction of the earth's field, indicates a positive force of 0.00117 C.G.S. The coincidence at about 70°, and not at a more displaced position as, for example, in fig. 3, indicates that the process is complete. It is therefore evident that, in order to obtain a maximum value of the shielding ratio, the shells must in the first instance be demagnetised very closely, with an initial current in the coils 1, 2, 3, even so large as 12 ampères, the maximum magnetic inductions produced by this current in the shells being relatively large. Even larger currents might be required if the polarisation in the shells were more important. The force 0.00117 C.G.S. unit at the angle 72° is regarded, in accordance with the argument in the first paper, as the true effect, within the internal space, of the earth's shielded field.

After the iron had been left for 21 days in the condition produced by the experiments which led to curve 10 (fig. 5), another exploration of the interior of the shield was conducted by rotating the inductor ring. In this manner the effect of resting of the material can be tested, and the result of the new experiment is shown in curve 10' (fig. 5). The change due to a considerable rest is seen by comparison of curves 10 and 10' to be very slight, and it is in a direction indicating that the field of the earth is tending to regain its original polarising effect. At the same time, the almost exact parallelism of the curves is an indication of the high degree of accuracy with which the inner space can be explored by an inductor adjusted in this manner.

It is interesting to notice that the current 0.751 ampère, which was used finally in the fourth coil in such a direction as to oppose the earth's field within the coil, is identical with the current used in the earlier paper, and, as was pointed out at the time, it is the current which just suffices to annul the force due to the earth\* in the hollow of the shield. The experiments, in fact, lead to the conclusion, stated in the introductory remarks in this

<sup>\* &#</sup>x27;Roy. Soc. Proc.,' A, vol. 92, p. 545 (1916).

communication, that an essential feature of the effective demagnetisation of the shells is the use of an enclosing current which will annul the direct action of the earth, so that reversal continually takes place in the whole magnetic induction at every point. Iron behaves in such a manner that a steady field and an alternating and diminishing field applied together leave a joint effect of permanent magnetism in the material. This conclusion has been obtained before\* in the case in which the steady field is due to a coil carrying current. It must now be extended to a small permanent field such as that of the earth, and the present effect is merely a manifestation of the same phenomenon on a smaller scale, but with important consequences on account of the very small magnetic effects which must be measured in the present experiments. The fact that it has not been noticed by earlier workers is probably due solely to the more limited degree of accuracy with which the larger fields employed by them could be, or needed to be, measured.

The importance of leakage due to the small air-spaces at the junctions of the shells, even after machining, requires some emphasis in so far as it affects the shielding produced. If it were entirely absent, the field in the interior, however small, should be uniform when polarisation of an irregular type is removed; and it should therefore be possible by the aid of residual magnetism, produced by a current of the proper amount applied to a magnetising coil, to so polarise the shells that the resultant field in the interior should be absolutely zero. But the leakage field is not uniform, and must, in fact, from obvious theoretical considerations be of some complexity, so that no simple arrangement of coils carrying currents can be devised which will, for internal points, completely annul this field. The experiments have shown that the machining of the shells has very greatly reduced the leakage, which is now of order 0.001 C.G.S. unit, instead of the original 0.006 unit. A portion of the original direct field, parallel to that of the earth, is, of course, due also to leakage, and this fact explains some of the reduction of this field from 0.0038 to 0.00117 unit.

For the purpose of comparison with the results obtained before the shells were machined, the curves 11, 12, 12' of fig. 5 are reproduced from the earlier paper. Curve 11 was obtained after the shells had been demagnetised from an initial current of 3 ampères in coils 1, 2, 3 in series, during such time as a current of 0.746 ampère was maintained constant in coil 4, and in opposition to the earth's field in the interior of the coil. Curve 11 was determined after the breaking of this steady current, and curve 12 after the current had been restored in the fourth coil, and reduced after the usual

<sup>\* &#</sup>x27;Roy. Soc. Proc.,' A, vol. 83, p. 1 (1909).

manner to zero. Curve 12' was observed under the same circumstances as curve 12, after an interval of four days, and shows the effect of a period of rest. The relation between 12 and 12' is identical with that between 10 and 10' described already.

It is, perhaps, unnecessary to remark at length upon the manner in which the more curious features of the curves obtained in the first paper have now received a satisfactory interpretation. In the testing of the shells as received originally from the foundry, the reversal of the internal force which was obtained was attributed to a possible polarisation of the shells produced by the earth's field during the process of cooling. In the light of the present experiments, it is apparent that the effect was, if not wholly, at least mainly, due to polarisation produced at the time of test. For the amplitude of the reversed internal force is 0.0038 C.G.S. unit when the initial demagnetising current in coils 1, 2, 3 is 4.7 ampères, and it is 0.008 due to demagnetisation from 12.5 ampères. In the latter case, the shells were highly polarised before demagnetisation. In the experiments of the earlier paper, before machining of the shells, a force of value 0.02 was observed after demagnetisation, as shown by curves x, y, z, in fig. 3 of the present paper, and this is in substantial agreement with the force observed when the shells were tested as received from the foundry. A more detailed examination does not appear to be required.

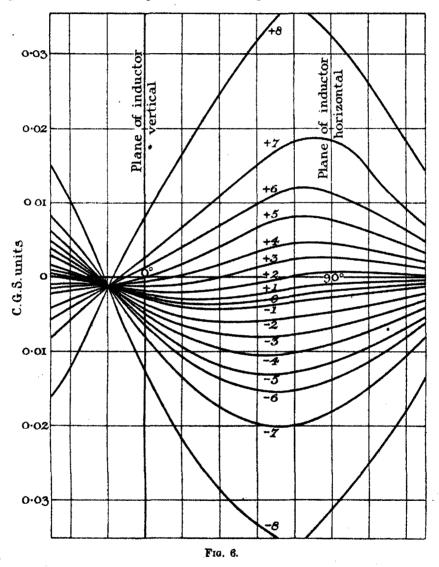
It is essential to success that the iron shall be demagnetised when free from the direct action of the earth's field. This approximate freedom from direct action can be secured sufficiently in practice by a somewhat wide range of current in the outer coil.

It is well known that if iron is subjected to a considerable magnetising force and then tested for permeability at a lower force, the permeability obtained is less than it would have been in the event of previous demagnetisation of the iron. The present experiments show that the earth's magnetic field produces a polarisation which by analogy should imply a higher permeability when removed. The increase of permeability which occurs in a specimen of iron demagnetised in a magnetic shield thus receives an interpretation in the light of these results.

# Some Effects Due to Residual Magnetism.

In the following experiments, currents of gradually increasing amount were passed through the fourth magnetising coil, in each case (a) positively, in order to assist the field of the earth within the shield, and (b) negatively, in order to oppose it. The force in the interior of the shield was determined by the inductor as a wave form in four cases:

(1) when any given current was flowing positively, (2) when that current was broken, (3) when the same current was flowing negatively, and (4) when this current was broken. These operations were performed for a sequence of currents. Fig. 6 exhibits a sequence of wave forms obtained



for the internal space. Those corresponding to the various positive currents are curves +1, +2, +3,..., whereas curves -1, -2, -3,..., relate to the corresponding equal negative currents. The values of the currents in ampères are given in the accompanying Table (Table I). The internal force

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Table

ا	1	•		,	-		-	,		
	Ampères ta fourth coil	ಶ	0 -0708.	0 .18T	.386. ⊃	0.283	0.822	1 .15.	1 :73.	
Angle.	Curve number, fig. 6,	0.	-	oqi	eri	4	ī,	9	7.	. œ
60	After application of— Positive current	1	081	82	981	130	123	133	801	74
	Negative current	+103	121	116	121	112	106	601	981	155
	Difference	(+17)	-1	4	+	+ 18	+ 17	\$\$ +	- 18	- 81
- 27	+	l	72	88	<b>8</b> 8	16	86	81	76	8
	1	- 91	11	92	<b>3</b> 5	<b>9</b> 8	001	8	79	88
	Difference	(-19	<u>م</u> د	+ 10	4	ب ب	∞ 1	6	99	91 +
රී	+	1	359	356	354	374	370	37.1	356	348
	1	- 358	350	352	354	359	377	698	863	65
	Difference	(+1)	6+	+	0	+ 15	1-	81	- 1	- 11
ô	+	1	629	630	621	639	651	999	619	576
	1	- 627	621	614	617	624	643	379	9	95.
	Difference	(2+)	œ +	9 +	+	+ 15	<b>∞</b>	+ 18	- 21	1.
27	+	ı	722	724	721	741	750	768	713	652
	1	736	718	732	714	718	737	746	149	767
	Difference	(-14)	4	89 +	+	+ 23	+ 13	83 +	98	-115
\$	+	1	869	669	069	705	723	752	682	288
	1	-724	269	069	675	683	708	90,	718	740
	Difference	(-31)		თ +	9 +	+ 23	+ 14	+	98	-152
SS SS	+	1	242	543	249	550	292	597	515	436
	1	1,588	240	243	532	521	535	260	603	587
	Difference	(-26)	-	+	<u>+</u>	62 +	- - - -	+ 37	88 	- 151
816	+	1	397	401	402	403	414	445	370	281
	1	83	405	4	382	381	394	401	406	449
	Difference	( <del>8</del> 3 – )	œ I	es 	+ 17	+ 22	08 +	88 +	98 -	- 168
8	+	1	330	320	307	317	815	337	088	213
	1	- 333	319	321	302	291	305	315	322	857
	Difference	(13)	+	<b>-</b>	63 +	92 +	+ 13	23 +	1	-144
17	+	1	255	258	246	244	242	258	213	160
	1	-260	255	248	241	258	228	255	000	285
	Difference	(-0)	0	+ 10	то +	- 14	+ 14	eo +	- 37	-125
182	+	1	161	157	151	144	135	144	116	86
		-161	159	157	152	130	125	136	146	186
	Difference	9	4	<b>-</b>	_ 	71 7	¥ 1	4	5	2

before these operations were commenced was that shown by curve o (fig. 3), which is reproduced in fig. 6, on a smaller scale, and again called curve o in the new figure. The permanent effect of these successive positive and negative magnetisations upon the curve o has been small in comparison with the magnitudes of the corresponding forces during the intervals of time in which the various currents were flowing. It is, however, not possible to exhibit on a small scale with clearness all the curves showing the permanent alterations in the internal force due to the successive temporary positive and negative magnetisations. But the ordinates of the resulting curves are shown in the Table in divisions of the galvanometer scale, and one such division represents  $5.06 \times 10^{-6}$  C.G.S. unit. The differences shown in brackets in the Table indicate the initial differences produced by the smallest applied current which was adopted. Differences without brackets are the effects of the reversal of the current. The first current applied in the case of each wave form had a positive sign.

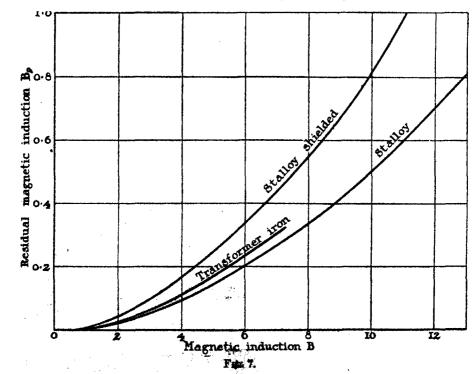
## The Effects of Hysteresis.

Fig. 6 and Table I illustrate some of the effects of hysteresis, which is, of course, the agency producing the residual magnetism introduced into the shells at the time of test. If a current be passed through the fourth coil and then broken, the hysteresis in the iron of each shell will cause, in varying degree, a certain residual magnetic induction which must produce an internal magnetic force superposed on the force already existing. In these experiments, this new force is negative, as indicated by curve o (fig. 6). After the application of the positive currents 1.73 and 3.95 ampères, corresponding to curves +7 and +8 of fig. 6, the internal force is diminished, showing that the new residual magnetism has produced a positive force. With currents of this magnitude, the polarisation begins to be strong. On the other hand, currents of magnitudes 0.583, 0.822, 1.15 ampères, as shown by curves +4, +5, +6, produce a contrary effect. Possible errors of observation make the differences in the case of currents 0.0708, 0.191 ampère, as in curves +2 and +3, less reliable, but, at the same time, the differences obtained have a pronounced positive tendency on the whole, and the effect cannot well be mistaken. The general conclusion derived from the Table can be summarised in the statement that for currents ranging between the values 0.365 and 1.15 ampères, there is a reversal in sign of the residual effects. The mean of these values is 0.75 ampère, which is the current most effective in neutralising the earth's field in the interior of the shells in the preceding set of experiments. The range of current is equal on either side of this value, and over the whole range there is, the current has a negative sign,

a rough approximate neutralisation of the earth's field. It is suggested, therefore, that this reversal in the sign of the residual effects is connected with the fact that the earth's field was operative during the present set of experiments, and that the reversal is, in fact, due to the presence of this field. This throws light upon the nature of the action of a steady field in preventing complete demagnetisation of a mass of iron.

Tests for hysteresis loss have recently been made in the case of the circular transformer iron stampings originally used as a magnetic shield by one of us,\* and the results are given in Table II. They are of special interest in this connection because the initial permeability of the material approximates very closely to that of the present spherical shells. It should be noticed that these stampings had not been magnetised previously except by the magnetic field of the earth, and that the specimen was exposed to this field during the test. The total volume of iron used was 23,440 c.c., and the average thickness of the stampings was 0.0613 cm. Each had internal and external diameters of 30.5 and 40.6 cm., and the cross-sectional area of the cylinder into which they were formed was 210 sq. cm.

In fig. 7, the residual magnetism  $B_0$  of this specimen is plotted in terms of the



value of  $B_{max}$  present during its production. For the purpose of comparison, the corresponding curves for a specimen of "Stalloy," or silicon-iron alloy, are shown in the same figure before and after treatment with the earlier form of shield described some time ago.\*

Table II.

	Maximum H.	Maximum B.	Perme- ability.	Residual magnetism B <sub>0</sub> .	Coercive force, H <sub>0</sub> (in 10 <sup>-6</sup> ).	Ergs per cycle per c.c. (in 10 <sup>-6</sup> )
Transformer iron	0.0000784	0.0109	148		Angele place of the St. 190 (Proper St. 1900)	
2	0.0001147	0.0170	148			Ī
	0 000284	0.0854	151			1
	0.000487	0.0682	150	:		1
	0.000806	0.128	158	0.00070	4.6	0.10
	0.00181	0.203	155	0.00076	4.95	0.3
i	0.00194	0.802	156	0.00092	5 -84	0.5
	0.00848	0.542	156	0.00206	13.2	2 · 2
	0.00724	1 .15	159	0.0074	56	15.8
	0.0148	2 .36	165	0.040	280	152
	0.0214	8.59	167	0.085	510	514
	0.0356	6.18	172	0 .244	1,500	2,150
Stalloy before treat-	0.00168	0 · 462	275			
ment in magnetic	0.00420	1.18	281	0.016	47	17 . 5
shield	0.00843	2.44	289	}		
	0 .0179	5 . 55	310	0.18	500	861
	0.0496	19.6	895	1 · 47	4,000	18,100
	0.0935	45.7	489	4.45	10,000	102,000
Stalloy after treatment	0 '00168	0 <b>-6</b> 8	405	0.0068	16	8 ·1
in magnetic shield	0.00420	1 .72	410	0.028	58	30.6
-	0.00848	8 .28	426	0.13	810	279
}	0.0179	8 .02	498	0.65	1,400	2,910
	0 '0496	86 .4	784	4.9	6,800	58,800
	0 .0935	88 .8	944	14.0	18,800	306,000

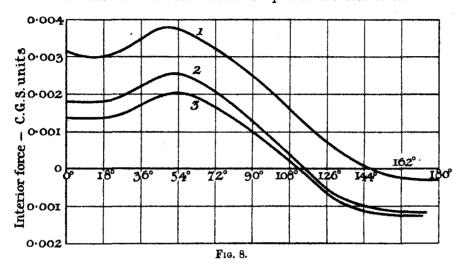
#### On the Effect of Sluling Brush Contacts.

When measuring the strength of an internal field of the order 0.002 C.G.S. unit, it was possible to cut out the extra resistance in the galvanometer and inductor circuit, and to obtain a deflection within the limits of the scale, and of such magnitude that the permanent set in the suspension fibre due to twist was still negligible. It was also possible to obtain readings of considerable accuracy when a resistance, so large as 10,000 ohms was added to the circuit. In fig. 8 the curves 1, 2, 3 were obtained with 10,000 ohms, 2000 ohms, and no added resistance respectively, and it will be noticed that the amplitude of the maximum ordinate at angle 54° is variable. Moreover, the ordinates at the angles 0° and 180° are not equal, as they should be,

<sup>\* &#</sup>x27;Roy. Soc. Prec.,' A, vol. 90, p. 179 (1914).

since we are dealing with a function which is periodic in regard to each half period.

If the ordinates at 0° and 180° are made equal in the case of each curve



by raising the horizontal axis, then the maximum ordinate is found to vary as shown in the following Table.

Table III.

Added resistance in ohms.	Maximum ordinate at 54°.							
	1.	2.	8.	4.	5.			
10,000 2,000 0	0 ·00208 0 ·00208 0 ·00181	0 ·00228 0 ·00228 0 ·00195	0 00205	0 ·00214 0 ·00192	0 ·00216 0 ·00184			

Comparison of the results obtained in any one experiment shows that the force is consistently smaller when no resistance is added. The forces with 10,000 and 2000 ohms additional resistance are substantially equal. Since the force was actually constant throughout any one experiment, we conclude that the displacement of the horizontal axis is connected in some way with the brush contact, and is a function of the current passing through the junction. The difference between the ordinates with no added resistance and either 10,000 or 2000 ohms added, after making the adjustment of the horizontal axis, is attributed to the damping of the instrument during the time of contact of the surfaces. This time depends upon the operator, and

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varies from ½ to ½ second. The inductor and its sliding contacts are described in an earlier paper.\*

# Summary.

- 1. The paper contains a further contribution to the study of the problems presented by the necessity for constructing a magnetic shield capable of reducing the earth's field to an order as low as 0.001 C.G.S. unit in a large space. The main problem, not treated in earlier papers, is that of residual magnetism in the various shells of the shield, and this problem is discussed in connection with exhaustive experiments in the present paper.
- 2. It is found that the ordinary process of demagnetisation of a mass of iron fails to be completely effective if, during the operation of the current, which is diminished by steps and continually reversed, a constant magnetic field such as that of the earth is present at the same time. This phenomenon has escaped notice hitherto, probably on account of the smallness of the earth's field, but it becomes prominent in experimental work involving the measurement of fields so small as that specified in (1).
- 3. This effect of the steady magnetic field is shown to be associated with a reversal of the residual effects of hysteresis in iron when tested in the earth's field by currents lying within a certain range in which they approximately annul the field.
- 4. It has been found possible to ensure complete removal of irregular polarisation or previous magnetic history of the shells, provided that during the preliminary demagnetisation of the shells the earth's steady field on them is annulled by a steady current of suitable amount enclosing the whole shield.
- 5. The magnetic shield described in earlier papers has now the degree of shielding which is required by theory in view of the known values of the permeabilities of its component shells. Its properties do not change appreciably with lapse of time.
- 6. The well known fact that iron polarised by a large force, and subsequently tested for permeability at a lower force, shows diminished permeability at the lower force gives, in combination with these results, an interpretation of the increase of permeability manifested by iron when tested within a magnetic shield.

<sup>\* &#</sup>x27;Roy. Soc. Proc.,' A, vol. 92, p. 540 (1916).

# Gravitational Instability and the Figure of the Earth. By J. H. Jeans, M.A., F.R.S.

(Received February 26, 1917.)

1. In a paper published in 1902, "On the Vibrations and Stability of a Gravitating Planet," I attempted to examine whether, owing to gravitational instability, an arrangement in concentric spherical shells might not be unstable for a planet of the size of our earth. It was not found possible to get exact results; progress only seemed possible by supposing that the problem would in its essentials be similar to a highly artificial problem in which gravitation was exactly annulled in the symmetrical configuration by the superposition of a countervailing field, so that in this state the matter was of uniform density and unstressed. The only possible justification for such an assumption was that I found myself unable to make any progress, either physically or mathematically, without it. Subject to this assumption, I found that, for a mass of the structure of our earth in its present state, the symmetrical configuration would undoubtedly be stable. It seemed likely, however, that in a past age in which the rigidity of the earth was considerably, although not enormously, less than it now is, the symmetrical configuration might have been unstable; the stable configuration would have been an unsymmetrical one, in which the surfaces of equal density were spherical but not concentric, so that the point of maximum density coincided neither with the centre of gravity nor the centre of figure of the earth's surface. It was suggested that traces of this unsymmetrical configuration might still be found in the arrangement of oceans and plateaux on the earth's surface.

In 1906, Lord Rayleigh,† in a paper "On the Dilatational Stability of the Earth," drew attention to the wide departure from actuality implied in my assumptions, and suggested a set of assumptions which had more justification in nature. Lord Rayleigh's suggestion was, in brief, that we might regard the symmetrical configuration as one in which the gravitational forces were balanced by hydrostatic pressures only. When disturbed, there is an additional stress superposed on to the hydrostatic pressure, and Lord Rayleigh suggested that this might be supposed connected with the additional strain—i.e., the strain above and beyond that in the initial configuration—by the ordinary elastic solid relations.

<sup>\* &#</sup>x27;Phil. Trans.,' A, vol. 201, p. 157.

<sup>† &#</sup>x27;Roy. Soc. Proc.,' A, vol. 77, p. 486.

These physical concepts, of course, presented a definite mathematical problem. Lord Rayleigh did not give the solution; this was attempted by Love in 1911 in his Adams Prize Essay, "Some Problems of Geodynamics." Love, however, assumes  $\rho_0$ , the initial density, and  $\lambda$ ,  $\mu$ , the elastic constants, to be constant throughout the mass. He remarks: "In a general theory we ought to take them to be functions of r, but as we cannot make any progress with a theory in which  $\lambda$ ,  $\mu$ , and  $\rho_0$  are functions of r, we shall treat them henceforward as constants." Subject to these assumptions, "the interesting result is found that, if the rigidity is rather small, compared with the resistance to compression, the body may be unstable in respect of displacements specified by spherical harmonics of the first degree, although stable as regards radial displacements. This result is distinctly favourable to the hypothesis that the division of the earth's surface into a landhemisphere and a water-hemisphere may be a survival from a past state in which a symmetrical arrangement of the matter about the centre would have been unstable."

The simple considerations brought forward in the present note seem, however, to show that when  $\lambda$ ,  $\mu$ , and  $\rho_0$  are allowed to take their natural values as determined by the configuration of the mass, this result is no longer true. The spherical symmetrical arrangement appears always to be stable.

2. If at any stage the symmetrical arrangement becomes unstable, the transition from stability to instability must be through a configuration in which one of the vibrations is of zero frequency, this configuration being a "point of bifurcation" in Poincaré's terminology. If instability sets in through first harmonic displacements, there must be two adjacent configurations of equilibrium for the same mass, one symmetrical, and the other derived from the symmetrical configuration by first harmonic displacements. The boundary of the latter configuration will be spherical and, as far as first order terms, its radius will be the same as that of the symmetrical configuration.

The question before us is accordingly whether there can, inside the same boundary, be two adjacent configurations, both being configurations of equilibrium, but one being symmetrical and the other unsymmetrical. We may consider the latter as being derived by distortion from the former.

Let  $p_0$  be the hydrostatic pressure in the symmetrical configuration, and let e, f, g, a, b, c, in the ordinary notation be the components of strain experienced by an element which was initially at pressure  $p_0$ . Following Lord Rayleigh's suggestion, the components of stress after distortion will be

$$P = -p_0 + \lambda \Delta + 2\mu e, \text{ etc.}, \qquad S = \mu a, \text{ etc.}$$
 (1)

where  $\Delta$  stands for e+f+g, the added cubical dilatation of any element of the mass produced by the additional strain. The condition that the strained configuration shall be one of equilibrium is expressed by three equations of the type

$$\frac{\partial \mathbf{P}}{\partial x} + \frac{\partial \mathbf{U}}{\partial y} + \frac{\partial \mathbf{T}}{\partial z} + \rho \frac{\partial \mathbf{V}}{\partial x} = 0, \text{ etc.}, \tag{2}$$

where V is the gravitational potential.

3. Consider first the simple case in which  $\mu = 0$ . Equations (1) reduce to

$$P = Q = R = -p_0 + \lambda \Delta, \qquad S = T = U = 0 \tag{3}$$

so that the system of stresses reduces to a pure hydrostatic pressure of amount  $p_0 - \lambda \Delta$ . Denoting this by p, equations (2) reduce to the usual hydrostatic equations

$$\partial p/\partial x = \rho \, \partial V/\partial x. \tag{4}$$

It follows in the usual way that the surfaces  $p = \cos$ , and the surfaces  $\rho = \cos$ , both coincide with the surfaces  $V = \cos$ .

The boundary condition, expressed in elastic solid form, is  $\Delta=0$ , so that at the boundary  $p=p_0=a$  constant, as is, of course, obvious also from the hydrostatic aspect of the problem. Thus, the boundary must be an equipotential, say  $V=V_b$ . This boundary is spherical, whence it follows that the external equipotentials must be a system of concentric spheres, and hence  $\partial V/\partial n$  is constant over the boundary. Both V and  $\partial V/\partial n$  are, of course, continuous on crossing the boundary.

Let the potential at any internal point in the unsymmetrical configuration be taken to be

$$V = V_0 + V_1 P_1,$$

where  $V_0$  and  $V_1$  are functions of r, and  $P_1$  is the first zonal harmonic  $\cos \theta$ . Then we must have, at the boundary,

$$V_1 = 0, (5)$$

$$\partial V_1/\partial r = 0. ag{6}$$

Let the density at any internal point be given by

$$\rho = \rho_0 + \rho_1 P_1$$

then, since the surfaces  $\rho = \cos s$ , coincide with the surfaces  $V = \cos s$ , we must also have at the boundary,

$$\rho_1 = 0, \tag{7}$$

$$\partial \rho_1/\partial r = 0. \tag{8}$$

From Poisson's relation  $\nabla^2 V = -4\pi\rho$ , we at once obtain

$$\frac{\partial^2 V_1}{\partial x^2} + \frac{2}{\pi} \frac{\partial V_1}{\partial x} - \frac{2}{\alpha^2} V_1 = -4\pi\rho_1. \tag{9}$$

From equations (5), (6), and (7), it follows that we must have

$$\partial^{\mathbf{y}} \mathbf{V}_{1} / \partial r^{\mathbf{y}} = 0, \tag{10}$$

at the boundary, and therefore also, as before,

$$\partial^2 \rho_1 / \partial r^2 = 0. \tag{11}$$

Equation (9) is true at all points of the mass: by successive differentiations with respect to r, we obtain

$$\partial^{8}V_{1}/\partial r^{8} = \partial^{4}V_{1}/\partial r^{4} = \dots = 0$$

at the boundary. Thus  $V_1$  and all its differential coefficients vanish at the boundary, so that  $V_1$  must vanish at all points inside.

This last step falls somewhat short of absolute mathematical rigour; indeed, there will probably be a few cases of failure of a highly artificial nature. We may, however, reflect that the initial distribution of density and potential in the mass will be determined by natural causes which will make it infinitely improbable that the arrangement of matter will correspond to one of the cases of failure; and, moreover, if at any instant the arrangement of matter was such that one of these cases of failure actually occurred, the slightest change in the physical conditions, such as might, for instance, be caused by cooling, would immediately alter this state of things.

We may get some idea of the degree of improbability involved, by considering what would be the actual procedure in discussing a definite concrete case. If p were given as a function of  $\rho$ , the value of  $V_1$  would appear as the solution of a certain differential equation. A first condition that the configuration should be one of equilibrium would be that  $V_1$  should vanish at the boundary—for instance, in the discussions given by Lord Rayleigh and myself, this equation took the form

$$J_{8/2}(\kappa a) = 0,$$

and the roots in a gave the radii at which the symmetrical configuration first became unstable. But the differential coefficients of  $J_{8/2}(\kappa a)$  do not vanish for these same values of a, and it would only be in a very special case in which  $J_{8/2}(\kappa a)$  happened to be replaced by a function which had one root in common with all its derivatives, such as Cauchy's function

$$e^{-1/(a-r)^2}$$

that we should have found a true point of bifurcation.\*

\* In Love's analysis ('Some Problems of Geodynamics') we obtain vibrations of zero frequency on putting  $p^2=0$ . On further putting  $\mu=0$ , his equation (22) on p. 95 reduces to  $9K_n=0$ , whence by §110 it follows that  $\Delta=0$  everywhere. Thus the supposed vibration of zero frequency reduces merely to a rigid body displacement, which of equipped does not in any sense mark a transition from stability to instability.

For practical purposes, then, we may conclude that when  $\mu=0$ , there is no solution except the spherically symmetrical one; excentric distributions are impossible, and the spherically symmetrical distribution is necessarily stable for first harmonic displacements.

4. When  $\mu$  is different from zero, the problem again reduces to examining whether there can be two adjacent configurations of equilibrium, the one being symmetrical and the other excentric.

It is, perhaps, almost obvious that rigidity must tend towards stability, so that if a mass cannot become unstable when  $\mu = 0$ , then a fortior it cannot do so when  $\mu$  is different from zero. A formal proof can be constructed as follows:—

Let the decrease of gravitational energy in passing from the symmetrical configuration to the excentric one be dG, and let the increase of elastic energy be dW. Then the condition that the excentric distribution shall be one of equilibrium is

$$dG = dW. (12)$$

The value of dW is, however, known to be

$$dW = \frac{1}{2} \left[ \left[ \left[ 2p_0 \Delta + (\lambda + 2\mu) \Delta^2 + \mu (\alpha^2 + b^2 + c^2 - 4fg - 4ge - 4ef \right) \right] dx dy dz \right]$$

where  $p_0$  denotes the hydrostatic pressure of the element now at x, y, z, when in its unstressed state. This can be put in the form

$$dW = dW_1 + dW_2$$

where  $dW_1$  contains all the terms which do not involve  $\mu$ , and  $dW_2$  is essentially positive. If the value of  $\mu$  had been zero everywhere, the increase of elastic energy would have been  $dW_1$ . Thus, from the result proved in § 3, it follows that  $dW_1$  must be greater than dG, so that a fortiori  $dW_1 + dW_2$  must be greater than dG, and equation (12) cannot be satisfied for any possible displacement.

5. It now appears that, for a natural mass under natural conditions, the spherically symmetrical configuration can never become unstable through first harmonic displacements. All such instability, proved or suspected, appears to be only a consequence of artificial conditions which were assumed, in the first instance by myself, with a view to making the analysis manageable, and the attempted explanation of the earth's dissymmetry of figure fails entirely.

# X-Ray Analysis of the Crystal-Structure of Rutile and Cassiterite.\*

By C. M. WILLIAMS, B.Sc., Fellow of the University of Wales.

(Communicated by Dr. E. H. Griffiths, F.R.S. Received March 1, 1917.)

The present paper deals with the results obtained in the investigation of the atomic structure of rutile and cassiterite by the X-ray spectrometer.

A detailed account of the method has been given by Prof. Bragg and his son, W. L. Bragg, in a series of papers communicated to the Royal Society. It consists essentially in allowing a narrow beam of monochromatic X-rays—in this case the rhodium rays—to fall on the face of the crystals, mounted on a spectrometer table, the axis of rotation of which passes through the face of the crystal. The beam is "reflected" by the atom planes parallel to this face, and thence passes into an ionisation chamber, containing methyl bromide in order to increase the ionisation current. The setting of crystal and chamber with regard to the incident beam corresponds to that for which ordinary light is reflected.

If  $\theta \doteq$  glancing angle of incidence; d = distance between the reflecting planes;  $\lambda =$  wave-length of the reflected wave; then Bragg has shown that the following formula holds—

 $2d \sin \theta = n\lambda$ , where n =order of the spectrum.

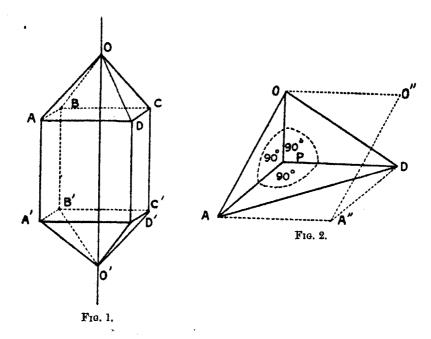
Hence, since the beam is mainly monochromatic, we shall get a maximum or "special" reflection at that angle for which the characteristic rhodium ray is reflected according to the above equation.

Thus, knowing  $\lambda$  for rhodium, we can obtain the spacings of the atom planes parallel to the various faces from a determination of the angles of special reflection from those faces.

Before proceeding to give results, it may be advantageous to describe the crystals so as to render the nomenclature clear.

Rutile (TiO<sub>2</sub>) and cassiterite (SiO<sub>2</sub>), with which is usually classed zircon (ZrSiO<sub>4</sub>), crystallise in the holohedral class of the tetragonal system. Fig. 1 represents a typical crystal of this group, and the crystallographic nomenclature may be conveniently explained with reference to it. Thus the plane OAD is called the 111 plane, and the intercepts of this face on a set of three mutually perpendicular axes give the ratios of the axes to which the crystal is referred.

\* An account of research work carried out in the Memorial Physical Research Laboratory of the University College of South Wales and Monmouthshire, Cardiff.



The symmetry of the crystal is such that it possesses:

- (a) A vertical axis of fourfold symmetry.
- (b) Four vertical planes of symmetry.
- (c) One equatorial plane of symmetry.

Hence the vertical axis is naturally taken to coincide with the axis of fourfold symmetry OO', and the two equal horizontal axes as parallel and perpendicular to AC.

Thus (fig. 2)-

The ratios of the axes are as PD: PA: PO.

For rutile , , 1:1:0.644.

For cassiterite , 1:1:0.67.

The other planes are referred to as follows:-

Plane.	Name.	
ACC'A' (fig. 1)	100	
<b>A</b> DD' <b>A</b> ' (fig. 1)	110	
OAA"O" (fig. 2)	101	
ABCD (fig. 1) or PDA (fig. 2)	001	

Both crystals have cleavage planes parallel to the 100, and also to the 110 faces, and are striated vertically on those faces.

The results of the determination of the angles of special reflection of the first order are given in the following Table:—

Crystal.	Plane.	Glancin	g angle.	Sin 0.	d.
			,		10 <sup>-8</sup> om.
Rutile	100	8	52	0.0674	4.495
	110	5	24	0 -0941	8 -225
1	001	11	56	0.2068	1 .467
ļ	101	6	58	0 .1218	2 .502
	111	4	U	0 .0698	4 .848
Cassiterite	100	8	80	0 0610	4 975
1	110	5	10	0.0800	8 -228
]	001	11	0	0 -1908	1 .590
Ì	101	6	87	0.1152	2 .684
į	111	3	37 P	0.0681	4 .818

Table I.

These angles were obtained by observing the position of special reflection, first on one side of the table and then on the other. Except in the case of the weak reflection from the 111 planes the chamber could be set to within a few minutes of the correct position, which defines the glancing angle to within about 2 or 3 minutes.

A comparison of the spacings of the three chief planes shows that we have for

- (a) Rutile .......  $d_{100}:d_{001}:d_{110}::1:0.325:0.717$
- (b) Cassiterite.....  $d_{100}:d_{001}:d_{110}::1:0.32:0.677$

It is at once noticeable that the spacing of the 001 planes is half what is to be expected from the crystal data.

Again, we notice that the spacing of the atoms in cassiterite is greater than that for rutile; the crystal is built on a larger scale. This is in agreement with the Theory of Molecular Volumes; in fact, given the molecular volumes of cassiterite and rutile, and also the angle of reflection from one, we can calculate the value of the corresponding angle from the other.

Thus if 
$$\alpha$$
 = distance between the 100 planes,  
 $\beta \alpha$  = , , 001 ,

The molecular volume is  $\beta \alpha^3$  and is proportional to  $M/\rho$  (M = mol. wt.;  $\rho$  = density).

If a<sub>1</sub> and a<sub>2</sub> refer to cassiterite and rutile respectively

$$\frac{\alpha_1}{\alpha_2} = \sqrt[3]{\frac{151}{6.9} \times \frac{4.18}{80}} = 1.03.$$

We may also calculate the number of molecules contained in the rectangular prism cut out between two basal planes by the 110, 110, 110, 110 planes taken consecutively.

If m = mass of H atom; M = mol. wt.;  $\rho = \text{density}$  of crystal; N = no. of mols.,

$$N = \frac{d_{110}^2 \cdot d_{001} \cdot \rho}{M \cdot m}.$$

For rutile 
$$M = 80$$
;  $\rho = 4.18$ . Hence  $N = 0.486$ .  
", cassiterite  $M = 151$ ;  $\rho = 6.9$ . ",  $N = 0.506$ .

Or, since  $d_{100} = \sqrt{2} d_{110}$ , then the number contained in the elementary volume is 0.972 and 1.01 for rutile and cassiterite respectively, each of which is very approximately equal to 1.

Bearing of the Results on the Structure of Rutile and Cassiterite.

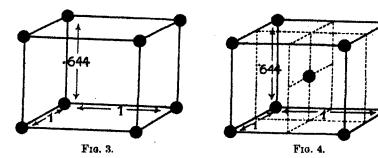
In applying the results to construct a model of the space-lattice representing the configuration of the atoms, complications arise owing to there being two kinds of atoms in the molecule. We have to bear in mind that the presence of the oxygen atoms may influence powerfully the spectra due Indeed, the Messrs. Bragg have adduced strong to the metal atoms alone. evidence in support of the view that an atom contributes to the amplitude of the reflected beam in proportion to its weight. With regard to the case under consideration, we have two isomorphous crystals in which the atomic weights of the metals composing them differ widely. Thus titanium has atomic weight 48, while that of tin is 119. Hence, while we might expect the oxygen in rutile to modify the spectra due to the metal atoms alone, even to the extent of cutting out some of the orders, we can fairly safely regard at least the position of the spectra given by cassiterite as being that characteristic of the lattice on which the metal atoms are built. matter of fact, the spectra in the two cases are remarkably similar.

Let us now attempt to construct a model which will explain the results obtained. From a consideration of the Bravais space lattices we are naturally led to try one of the two lattices characterising the tetragonal system of the form and dimensions shown in the diagram (for rutile), figs. 3 and 4.

It might at first sight be supposed that the ratio of  $d_{100}$  to  $d_{110}$  would decide between them; for in fig. 3  $d_{100} = \sqrt{2d_{110}}$ , while in fig. 4  $d_{100} = d_{110}/\sqrt{2}$ .

Owing, however, to the ambiguity in choosing the horizontal axes, this criterion does not avail.

But an examination of these two lattices shows that neither will explain



all the results. For taking fig. 3, we note that we have to associate 2 molecules with each point of the lattice as shown by the above calculation. Assuming 2 molecules associated with this elementary volume and knowing  $\theta_{100}$  we can calculate the angles of reflection from the other faces.

The disagreement between this theory and experiment is shown below for rutile:—

Face.	Calculated.	Observed		
	• /	0 /		
110	5 20	5 24		
001	5 55	11 56		
101	7 . 0	6 58		
111	7 58	4 0		

Table II.

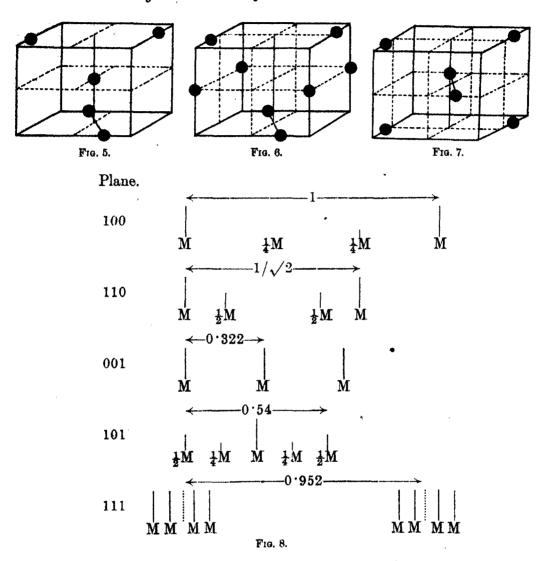
Striking differences occur in the case of the 001 and the 111 planes, where we notice that the calculated values are half and double the observed values respectively. Similar objections may be urged against fig. 4.

Any lattice selected must not only give the right spacing, but also the right amount of mass per elementary volume; while, in addition, it must conform to the symmetry of the crystal as a whole, namely, the holohedral class of the tetragonal system.

I'wo lattices, or possibly three, appear to satisfy the requirements of the problem. They are shown in figs. 5, 6, and 7.

The arrangement of the planes and relative spacings of the reflecting planes for fig. 6 are shown in fig. 8.

In order to test these lattices further we may examine the intensities of the different orders.



The method of determining the ratios was to set the crystal and chamber for a reflection, using a narrow incident beam, the slit of the chamber being sufficiently wide to take in the whole of the reflected radiation. The ionisation current was determined for all positions in the neighbourhood of the maximum by turning the crystal through successive small steps. The chief difficulty is due to the variation in intensity of the source. In order to obviate this as much as possible, a second slit was cut in the lead box containing the X-ray bulb. The beam issuing through this was reflected by a crystal into another ionisation chamber, the electrode of which could be

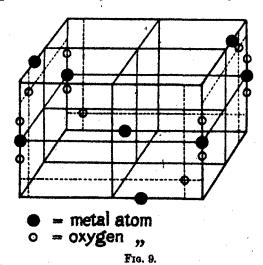
connected to the electroscope at will. Thus, on exciting the bulb, two reflected beams of characteristic rays passed into the separate chambers at the same time. On turning off the rays each electrode was connected in turn to the electroscope (in practice one was connected permanently to it), and the ionisation currents in the two chambers determined. Thus a fairly reliable check on the variations of the source was obtained.

To obtain a comparison of theoretical values with those observed (Table III), it is necessary to make assumptions in two directions:—

- (1) The scattering power of an atom: we shall assume that an atom contributes to the amplitude of the reflected beam in proportion to its mass—an assumption well justified by the Bragg results.
- (2) We have to assume a rate of decline of the intensities for successive orders for a set of precisely similar planes: we shall adopt the ratio given by W. L. Bragg for a normal order, namely 100:20:7, though it is quite possible that the ratio might depend on the crystal, and may not be the same for rutile as for cassiterite. We may note in this connection that Vegard obtained two different ratios for the normal order from different faces of a silver crystal.

Turning now to the configuration of the oxygen atoms, we notice that the intensity in the second order of the 100 spectrum of rutile is below normal. Hence it would appear that the oxygen atoms lie in planes parallel to the 001 planes, and tend to weaken the second order of the 001 spectrum. Bearing this in mind, let us attempt to associate two oxygen atoms with one metal atom. We then get the configuration shown in the diagram (fig. 9).

In attempting to form a comparison between theory and experiment, we



have to remember that the comparison must necessarily be of an empirical character, owing both to the assumptions made and to the difficulty of comparing the ratios experimentally.

In view of the above considerations, a very close agreement between theory and experiment cannot be expected.

The following results show the agreement obtained by taking the lattice represented by fig. 9, assuming—

- (1) That the metal atom between two consecutive 100 planes is displaced 0.403d and 0.375d for rutile and cassiterite respectively.
- (2) The horizontal displacement of the oxygen atom is 0.111d from the nearest 100 plane.
- (3) The distance between the metal 001 planes and the nearest oxygen plane is 0.25d and 0.32d for cassiterite and rutile respectively.

Crystal.	Plane.		1st order.	2nd order.	3rd order.
Cassiterite	100	Calculated	100	26	12
1		Observed	100	25	18
	110	Calculated	100	58	40
		Observed	100	50	25
	001	Calculated	100	16	Not observed
		Observed	100	19	
Rutile	100	Calculated	100	27	8
		Observed	100	88	16
	110	Calculated	100	49	10
		Observed	100	50	20
	101	Calculated	100	80	Not observed
• •		Observed	100	80	Not observed
	. 001	Calculated	100	12	
		Observed	100	10	Not observed
İ	111	Calculated	40	100	30001.00
1		Observed	50	100	Not observed

Table III.—Comparison of Intensities.

On the whole, there is a general agreement between the calculated and observed values of the intensities, and the calculated values are sufficient to account for the variation in the observed intensities of the spectra. As regards the other two lattices (figs. 5 and 7), it may be stated that they do not give an approximate agreement between the calculated and observed intensities.

The model presents many interesting features:-

- (1) It possesses the full symmetry of the holohedral class of the tetragonal system.
  - (2) It has a tetragonal screw axis.
  - (3) Both the 100 and the 110 planes are indicated as cleavage planes.

- (4) We note also that, in a sense, the crystal is enantiomorphous, two parts being obtained by a reflection across a 100 plane. This is interesting, on account of the fact that Bravais considered that crystals which showed twinning, such as that peculiar to rutile and cassiterite, to be of this character.
- (5) The peculiar vertical arrangement of the metal atoms in the direction parallel to the axis may possibly be connected with the striations observed on the vertical faces.

Note.—After the above observations had been made and embodied in a paper, results obtained by a similar method were published by Dr. Vegard\* on the structure of this group of crystals. His observations were in agreement with most of those given above, but differed in one or two vital respects, namely, the position of the reflections from the 100 and 111 faces, his values being twice as great as those given above. It was therefore thought highly advisable to repeat the observations on this point. For this a new X-ray tube had to be procured. Owing, however, to the war, considerable delay was caused, which prevented the confirmation being undertaken earlier. When, indeed, this became possible, all doubts about there being a reflection from the 100 face, as given above, were at once dispelled. As regards the reflection from the 111 faces, reflection at the angle stated above is quite definite in the case of rutile, though for cassiterite it is very small; still, calculation shows that this should be so.

It will be seen that these half-angle reflections can find no place in the model suggested by Vegard. It may be further noticed† that this model satisfies the crystal symmetry only on the assumption that certain elements of optical symmetry are of the nature of statistical effects, while the smaller wave-length of X-rays reveals an actual absence of these elements.

The good agreement obtained by Vegard between calculated and observed intensities depends partly on his assumptions of a different normal order (100:30:12) for cassiterite and zircon from the more ordinary ones (100:20:7) adopted for rutile. It may be pointed out, with respect to the unusual values (100:50) found by Vegard for the presumably normal order in the case of the 111 planes of silver, that narrowing the slit changed the ratio to 100:35. Without knowing the exact details of the experimental arrangements, it is difficult to say what the precise meaning of this change may be; it may be noted that the glancing angles for the 111 planes are smaller than those for the 100 planes, and it is not difficult to see that, with

<sup>\* &#</sup>x27;Phil. Mag.,' July, 1916.

<sup>†</sup> Loc. cit., p. 81.

small glancing angles, under certain arrangements of the apparatus, an excessive slit width would lead to a fictitiously high ratio of the second to the first order spectrum.

The crystals used in the above investigation were excellent specimens, lent me by Dr. Hutchinson, of Cambridge, to whom my best thanks are due. I am also indebted to Prof. Bragg for the very kind interest he has shown in the work, and to Principal Griffiths, for his sympathy and kindness in considering my requirements. Further, I desire to express my heartiest thanks to Captain J. H. Shaxby for the valuable guidance and assistance he has rendered me throughout the work.

The Composition of the X-Rays from Various Metals.

By G. W. C. KAYE, M.A., D.Sc., Gaptain R.E. (T.).

(Communicated by Dr. R. T. Glazebrook, F.R.S. Received March 13, 1917.)

(From the National Physical Laboratory.)

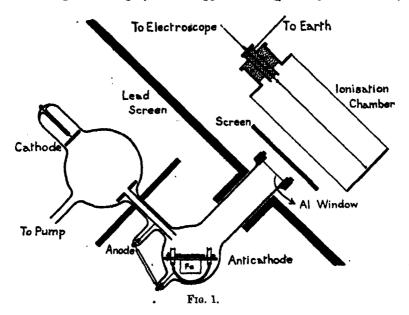
In a paper published in the 'Philosophical Transactions'\* in 1908, the writer described some experiments on the X-rays emitted by a variety of metals when used as anticathodes in an X-ray bulb. Among the results established was the homogeneity of a large proportion of the X-rays when the bulb was very "soft." The absorption curves of the several homogeneous radiations revealed their identities with the characteristic "secondary" radiations which Barkla and Sadler had then recently discovered.

The experiments described in the present paper are an extension of the above, and were carried out partly at the Cavendish Laboratory in 1908 and partly at the National Physical Laboratory just prior to the war. The writer's military duties have prevented the continuation of the work, and the results are now put on record in the hope that they may help to further the progress of the subject, to which the more precise method of the crystal-spectrometer has given a great impetus from a different point of view.

#### Apparatus,

The apparatus employed is sufficiently explained by fig. 1, which is approximately to scale. As in the earlier experiments, the various anti
\* Series A, vol. 209, p. 123.

cathodes were mounted on a trolley, which could be magnetically propelled. A coil-discharge was employed, the applied voltage being indicated by an



alternative spark-gap between polished balls 2.5 cm. in diameter. For balls of this size and spark-gaps in the neighbourhood of 1 cm., the expression

$$V = 30,000d + 2000$$

gives approximately the voltage V, corresponding to a spark-length of d cm.

The X-rays passed out of the tube through an aluminium window (2 cm. diameter and 0 0065 cm. thick), and were received by an ionisation chamber, the front face of which was about 3 cm. from the window. The depth of the chamber was 4 cm.; the sides were of thin aluminium leaf. A Wilson tilted electroscope was employed to measure the ionisation currents.

The quality of the X-rays was tested by absorption screens inserted between the window and the ionisation chamber. Metal leaf was used for the thinnest screens.

For details of the various experimental precautions, the writer's earlier paper on the subject may be consulted. In the present paper, the radiations dealt with are those from iron, nickel, copper, aluminium, and platinum.

# Logarithmic Absorption-curves.

The absorption-coefficient  $\lambda$  of a substance is defined by the expression  $I_d = I_0 e^{-\lambda d}$ , where  $I_0$  is the initial intensity of an X-ray beam and  $I_d$  the

intensity after transmission through a screen of the substance of thickness d. Accordingly, if the thickness of screen (as abscissa) is plotted against  $\log_{10} (I_d/I_0)$ , the slope of the tangent to the curve at any point gives (when multiplied by 2·3) the value of  $\lambda$  at that point. For ordinary heterogeneous X-rays,  $\lambda$  diminishes as d increases, but, if the rays are homogeneous, the graph is a straight line.

### Analysis of the Log-absorption Curves.

The method employed in the present experiments was gradually to cut down the X-rays until the log-absorption curve showed that the residual rays were homogeneous or nearly so. This "end-radiation" was subtracted (graphically) from the whole radiation by producing backwards the final straight part of the absorption curve. A new log-absorption curve was then plotted, employing as ordinate the log of the intensity-difference derived as above. The resulting graph proved in practice to be either (a) a straight line throughout its length, or (b) a curve merging into a straight line as the thickness of screen increased. In the latter event, the process of subtraction was applied again.

The underlying notion was to ascertain whether by such analysis the absorption curves could be made to reveal the presence of characteristic radiations. The justification for the method depends upon its success, for it is possible to express, with very fair accuracy, almost any normal type of absorption curve as the sum of two or three exponentials. If such components have a physical reality, they will be found to recur in the different absorption curves under varying conditions.

With low discharge voltages on the tube, the dilution of the characteristic rays by general radiation is slight, and the existence of an appreciable amount of a characteristic radiation is usually betrayed before analysis by a perceptible flattening of the absorption curve over part of its course. But with higher voltages the conditions change, and the method is not so easy unless the accuracy of the measurements and of the graphical analysis is high. The present experiments are not offered as final, but they do, at any rate, indicate that by such means the detection of component radiations is possible provided they are present in appreciable amounts. That such homogeneous components may be expected is shown by the fact that the lines in high-frequency spectra are now known to be not nearly so limited in number as was at first believed.

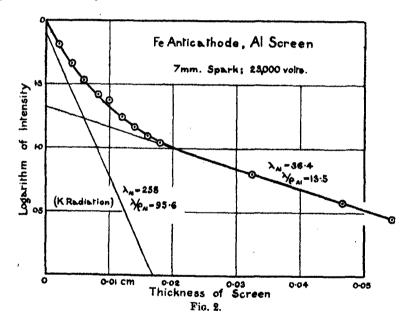
In those cases where the method of graphical analysis is profitable, there is never any difficulty in "spotting" the K and L characteristic radiations; their absorption-coefficients always come out sufficiently near to the accepted

values. Incidentally, the method also reveals the proportion of each radiation present in a beam of rays.

In all the log-absorption curves illustrated in this paper, the original curve is indicated by a heavy line, and the resulting components by thin lines. Most of the radiations were analysed by screens of aluminium, platinum, and copper. In general, the curves for platinum screens are similar to those for aluminium screens; those for copper screens do not always share their common characteristics.

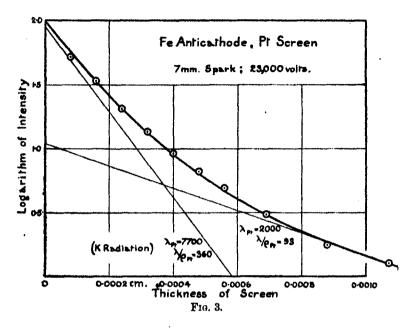
#### Iron Radiation.

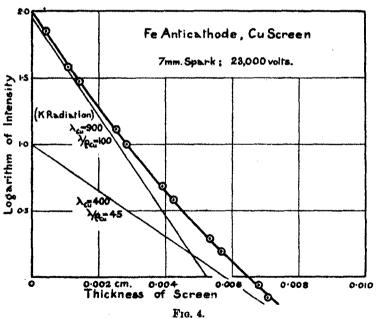
Figs. 2, 3, 4 show the log-absorption curves of iron radiation in screens of aluminium, platinum, and copper respectively. In each case the voltage applied to the X-ray tube was 23,000.



Aluminium Screens.—The absorption curve (fig. 2) is practically straight for screens thicker than 0.02 cm. There is about 20 per cent. of this homogeneous end-radiation ( $\lambda/\rho_{Al} = 13.5$  c.g.s.), and analysis reveals that the remaining 80 per cent. consists of iron K-radiation ( $\lambda/\rho_{Al} = 95.6$ ).

Platinum Screens.—Fig. 3 similarly displays the absorption curve and its resolutes for screens of platinum. There is about 90 per cent. of Fe K-radiation ( $\lambda/\rho_{\rm Pt}=360$ ) and 10 per cent. of an end-radiation with  $\lambda/\rho_{\rm Pt}=93$ .



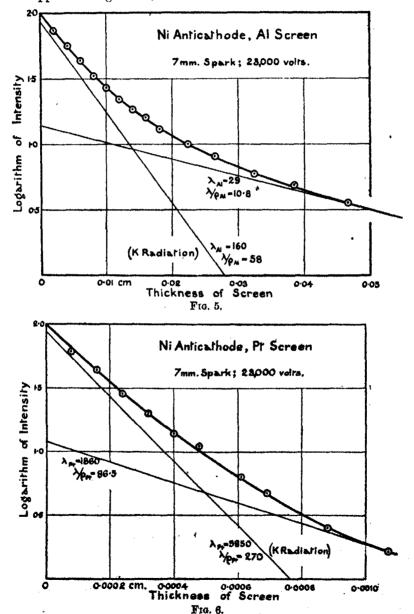


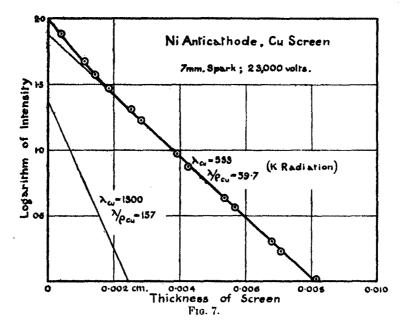
Copper Screens.—The analysis of the log-absorption curve (fig. 4) again gives about 90 per cent. of Fe K-radiation ( $\lambda/\rho_{\rm Cu}=100$ ) after deducting 10 per cent. of a harder end-radiation with  $\lambda/\rho_{\rm Cu}=45$ .

Figs. 2, 3, and 4 are thus very similar to each other and lead to almost identical results.

## Nickel Radiation.

Figs. 5, 6, 7 are a corresponding set of curves for nickel radiation, again with an applied voltage of 23,000.





Aluminium Screens.—Just as with iron radiation, two components represent the absorption curve (fig. 5), viz., 86 per cent. of nickel K-radiation  $(\lambda/\rho_{A1} = 58)$  and 14 per cent. of end-radiation with  $\lambda/\rho_{A1} = 10.8$ ). This agrees closely with Rawlinson's figures,\* who analysed nickel radiation generated under a voltage of 30,000, into 79 per cent. of K-radiation and 21 per cent. of rays with  $\lambda/\rho_{A1} = 10.4$ .

Platinum Screens.—The absorption curve (fig. 6) is like that for aluminium screens, and we find after subtracting 12 per cent. of end-radiation with  $\lambda/\rho_{\text{Pt}} = 86.5$ , that the remaining 88 per cent. is entirely Ni K-radiation ( $\lambda/\rho_{\text{Pt}} = 270$ ).

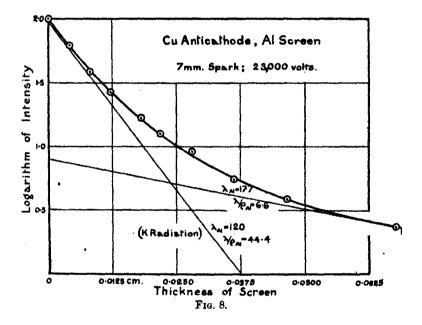
Copper Screens.—Thus aluminium and platinum screens absorb iron and nickel radiations in similar fashion, but we now find that copper screens treat the two radiations very differently. With nickel radiation, the absorption curve (fig. 7) is, except for the thinnest screens, straight throughout its length, revealing about 75 per cent. of Ni K-rays. Not even when the radiation was reduced to ½ per cent. was there any trace of the end-radiation of figs. 5 and 6, and we are led to infer that the end-radiation has been abnormally absorbed and transformed into copper K-radiation, the absorption-coefficient of which does not differ very greatly from that of nickel K-radiation.

On the other hand, a soft component ( $\lambda/\rho_{\rm Cu}=157$ ) has now made its \* 'Phil. Mag.,' p. 274, August, 1914.

appearance to the extent of 25 per cent. This may be another characteristic radiation for which Al and Pt screens are specially absorbent. It is very probably mixed with the softer copper radiation ( $\lambda/\rho_{\text{Ou}}=100$ ) referred to below, which has been excited in the screen by the Ni rays from the bulb. Iron radiation is a good deal softer than Ni radiation and the consequent inability of the Fe radiation to excite any such copper component would be an explanation of its absence in the corresponding absorption curve in fig. 4.

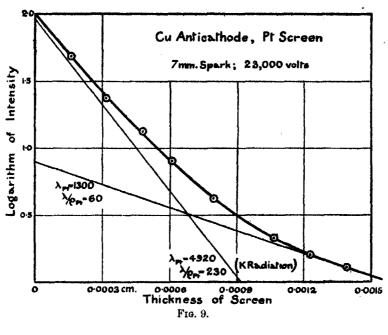
# Copper Radiation.

Figs. 8, 9, and 10 give the graphs for copper radiation. The applied voltage in each case was again 23,000.



Aluminium and Platinum Screens.—Figs. 8 and 9 show the log-absorption curves of Cu radiation in Al and Pt respectively. Subtracting 8 per cent. of end-radiation reveals in each case the copper K-radiation as making up the rest of the rays. The curves are, therefore, precisely similar in type to figs. 2 and 3 for Fe radiation, and 5 and 6 for Ni radiation.

Copper Screens.—If now we turn to fig. 10, we find that copper screens treat nickel and copper radiations very similarly. Just as with Ni radiation (fig. 7), but unlike Fe radiation (fig. 4), the end-radiation completely disappears and is replaced by Cu K-radiation. At the same time a new and softer component appears with a  $\lambda/\rho_{\rm Cu}$  of about 100.



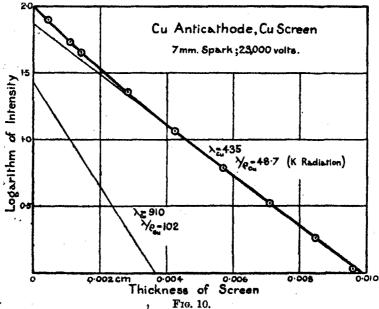
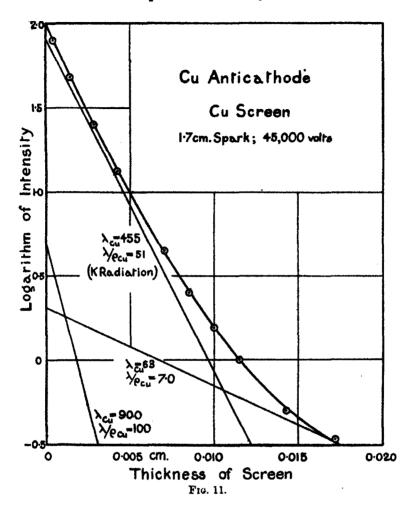


Fig. 11 shows the corresponding curve with a higher voltage (45,000) on the tube. Both the preceding radiations are again revealed after subtracting a small amount of end-radiation.



The experiment was repeated for a number of applied voltages. In each case the two radiations were found to be present. Table I gives the results, and it will be seen that the proportion of K-radiation increases with the voltage while that of the softer radiation diminishes. It would certainly be of great interest to extend the limits of voltage employed. According to Whiddington, at voltages below about 10,000 no K-radiation is generated, and it is a matter for enquiry to see if the softer characteristic component here referred to plays a prominent part under such conditions. The calculated wave-length of this softer component is about  $2\times 10^{-8}$  cm. So far as I know, it has not been detected spectroscopically.

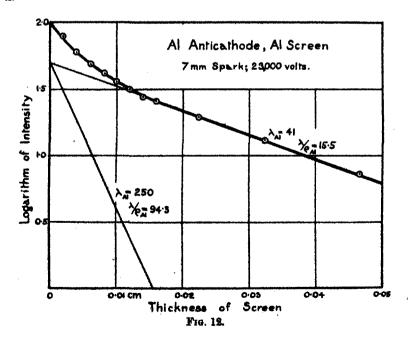
Table I.

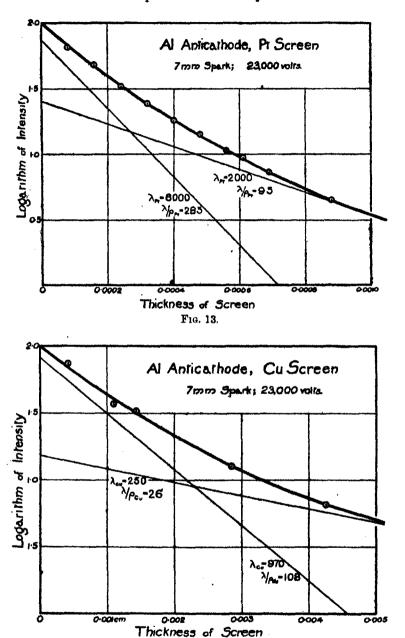
Spark.		Radiation.		
	Volta.	$\lambda/\rho_{\rm Cu} = 100.$	$\lambda/\rho_{\mathrm{Cu}} = 58,$ K-radiation.	End-radiation.
mm.	10.000	per cent.	per cent.	per cent,
2 .5	10,000	82 26	68 74	0
10	28,000 32,000	26	76	0
17	45,000	16	82	2 p.c. of $\lambda/\rho_{Cu} = 1$

## Aluminium Radiation.

Figs. 12, 13, 14 give the absorption curves for Al radiation when passed through Al, Pt, and Cu screens. The voltage is 23,000.

Aluminium Screens.—The absorption curve (fig. 12) may be analysed approximately into 50 per cent. of end-radiation ( $\lambda/\rho_{\rm Al}=15.5$ ), and 50 per cent. of a radiation having  $\lambda/\rho_{\rm Al}=94.3$ . Both values are rather low as there is a small proportion of penetrating radiation present. For example, the rays which remain after passage through a 1 mm. screen of Al have a  $\lambda/\rho_{\rm Al}=$  of about 1.





Platinum Screens.—Subtracting end-radiation  $(\lambda/\rho_{Pt} = 95)$  amounting to about 25 per cent. of the total radiation, the remaining 75 per cent. may be represented by a straight line radiation having  $\lambda/\rho_{Pt} = 285$ .

Fig. 14.

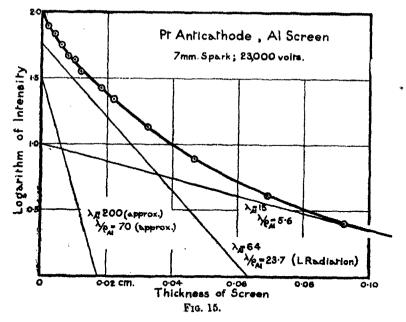
Copper Screens. - Subtracting the end-radiation (15 per cent. in all) with a  $\lambda/\rho_{\rm Cu} = 26$ , the remainder can be represented by a homogeneous radiation with  $\lambda/\rho_{Cu} = 108$ .

The above results on aluminium radiation are offered only as tentative.

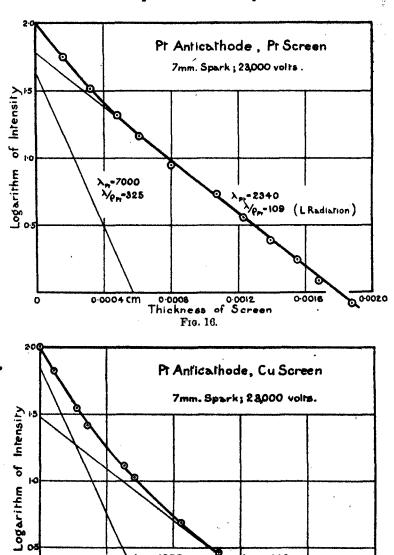
#### Platinum Radiation.

Figs. 15, 16, 17 deal with platinum radiation generated under a voltage of 23,000.

Aluminium Screens.—Fig. 15 betrays little indication of homogeneity until 10 per cent. of end-radiation  $(\lambda/\rho_{A1} = 5.6)$  is deducted, when a component consisting of 60 per cent. of Pt L-radiation ( $\lambda/\rho_{A1} = 23.7$ ) clearly reveals itself. Admixed with this is 30 per cent, of another and softer component which betrays its existence with the thinnest screens. Further analysis shows that this latter radiation is homogeneous and has a  $\lambda/\rho_{A1} = 70$ (approx.).



Platinum Screens.—In fig. 16, the end-radiation has disappeared, and the homogeneity of much of the radiation is apparent. There is no evidence of the presence of a harder type of ray even though the initial intensity is cut down to nearly ½ per cent. The curve is readily resolvable into 60 per cent. of Pt L-radiation ( $\lambda/\rho_{\rm Pt} = 109$ ) and 40 per cent. of a softer homogeneous component with  $\lambda/\rho_{\rm Pt} = 330$ .



Thus both Al and Pt screens agree in indicating the existence of two homogeneous beams in Pt rays, one the L-radiation, the other with an absorption coefficient three times as large.

Fig. 17.

0-004 Thickness Cu 440

oos Screen

of

Ypcu = 49.3

0-008

0-010

λ<sub>c4</sub>=1250

(LRadiation)

O-OOR CM.

Absorption curves obtained at higher and lower voltages, using Pt screens, disclosed the two components in each case. The results, which are given in Table II, show that with a low voltage on the tube more than half the X-rays consist of the softer component. An increase in the voltage leads to an increase in the amount of L-radiation, and a decrease in that of the softer radiation. Calculation gives a wave-length for the latter of about  $2.5 \times 10^{-8}$  cm.

Spark gap.		Radiation.		
	Volts,	$\lambda/\rho_{\mathrm{Pt}}=330.$	$\lambda/\rho_{\mathrm{Pt}} = 110$ L-radiation	
mm.	***	per cent.	per cent.	
4.	14,000 23,000	68* 40	87	
10	<b>82</b> ,000	37	68	

Table II.

Copper Screens.—In fig. 17 the absorption curve is built up of 30 percent. of end-radiation ( $\lambda/\rho_{Cu} = 49$ ) and 70 per cent. of Pt L-radiation ( $\lambda/\rho_{Cu} = 140$ ).

We have here an example of the importance of the choice of screen, for whereas a Pt screen allows nothing harder than the L-radiation to pass, a Cu screen allows nothing softer than the L-radiation to pass. This behaviour on the part of copper has been noticed by Bragg\* in his spectroscopic work; he remarks that the A peak of Pt is completely wiped out by a copper screen.

#### Ordinary X-Ray Bulbs.

A good many attempts have also been made to resolve the absorption curves obtained by using Al screens and ordinary X-ray bulbs (with platinum anticathodes) excited by considerable voltages. The writer's experience goes to show that in such cases the end-radiation, even after it is cut down to ½ per cent. or less, is never really homogeneous. It may, however, be taken as such for the purposes of approximate analysis. Such analysis almost always reveals the presence of Pt L-radiation. In the case of one tube worked at 30 mm. spark, there was 40 per cent. of L-radiation in the rays transmitted through the glass walls of the bulb; in the case of another at 85 mm. spark, 37 per cent. Most tubes also reveal the presence of a

<sup>\*</sup> Probably another and even softer component present as well.

<sup>\* &#</sup>x27;Roy. Soc. Proc.,' A, vol. 89, p. 434, November, 1913.

component having  $\lambda/\rho_{A1} = 7.4$ , in proportions which increase with the voltage, at any rate, within a moderate range.

The extent of the work was not competent to throw doubt on the prevailing view that the bulk of the X-rays from a bulb worked under voltages such as obtain in medical practice consists of other than general heterogeneous radiation.

### Summary.

The X-rays from a bulb-excited by low voltages (10,000 to 50,000 volts) are rich in the characteristic radiation of the anticathode. In the case of iron, nickel and copper, the amount of K-radiation lies between 80 and 90 per cent. In the case of platinum the proportion of L-radiation is from 40 to 60 per cent. Evidence of characteristic radiations softer than the K and L-radiation has been obtained.

The writer has perforce had to content himself with little more than setting down observations. For the preparation of the diagrams he is greatly indebted to Mr. W. F. Higgins, B.Sc.

# On Magnetic Inertia.

By George W. Walker, M.A., A.R.C.Sc., F.R.S., formerly Fellow of Trinity College, Cambridge.

#### (Received March 13, 1917.)

In the course of some investigations with regard to the Earth's magnetism, it occurred to me that a magnetised body must possess magnetic inertia in virtue of its magnetisation, just as an electrified body possesses electric inertia. I am not aware that this has been considered before, nor have I seen any calculation of the amount to be expected.

The method of dimensions shows that the magnetic inertia of a body of magnetic moment m should be a numerical multiple of  $m^2a^{-3}C^{-2}$ , where C is the velocity of radiation and a a linear dimension of the body (e.g., the radius, in the case of a sphere).

The problem may be investigated and the numerical factor determined by the same general method used for electric inertia.\* Consider a conducting sphere of radius  $\alpha$  uniformly magnetised with magnetic moment m.

\* 'Roy. Soc. Proc.,' A, vol. 77, p. 260 (1906), and 'Phil. Trans.,' A, vol. 210, p. 145 (1910).

(1) Let the sphere be magnetised parallel to the axis of a. When the sphere is at rest the magnetic forces are given by

inside 
$$(\alpha, \beta, \gamma) = -ma^{-3}(1, 0, 0)$$
,  
outside  $(\alpha, \beta, \gamma) = -mr^{-3}(1, 0, 0) + 3mwr^{-5}(x, y, z)$ .

Thus the tangential component of  $(\alpha, \beta, \gamma)$  is continuous at r = a, and the apparent surface density is  $\sigma = 3 m x a^{-4} / 4 \pi$ .

Now, let the sphere move under the action of a mechanical force so that the displacement along the axis of x at any time is  $\xi$ . The appropriate forms to be assumed for the field outside are (cf. loc. cit.):

$$(\alpha, \beta, \gamma) = -mr^{-3}(1, 0, 0) + 3mxr^{-5}(x, y, z) + Cxr^{-5}(1, 0, 0) (r^{3}\chi''' + 3r^{2}\chi'' + 6r\chi' + 6\chi + 6\xi m/C) + Cr^{-5}(x, y, z) (r^{2}\chi'' + 3r\chi' + 3\chi + 3\xi m/C) - Cr^{2}r^{-7}(x, y, z) (r^{3}\chi''' + 6r^{2}\chi'' + 15r\chi' + 15\chi + 15\xi m/C) (X, Y, Z) = Cxr^{-5}(0, -z, y) (r^{2}\chi''' + 3r\chi'' + 3\gamma'),$$

where  $\chi$  stands for  $\chi(Ct-r)$ 

Hence the electrodynamic force is

$$(X', Y', Z') = Cxr^{-5}(0, -z, y)(r^2\chi''' + 3r\chi'' + 3\chi' + 3\xi m/C^2).$$

We are at liberty to assume that inside

$$(\alpha, \beta, \gamma) = -ma^{-3}(1, 0, 0),$$

but we must suppose that the surface r = a is the seat of electric currents given by

$$(u, v, w) = Cxa^{-6}(0, -z, y) P.$$

Now this current is determined by the discontinuity of the tangential component of  $(\alpha, \beta, \gamma)$  at r = a.

Hence 
$$4\pi P = -(a^3 \chi''' + 3a^2 \chi'' + 6a \chi' + 6 \chi + 6 \xi m/C).$$
 (1)

The tangential component of X', Y', Z' vanishes at r = a if

$$3\xi m + C^2(a^3\chi''' + 3a\chi'' + 3\chi') = 0,$$

which is satisfied by

$$3\xi m + C(a^3\chi'' + 3a\chi' + 3\chi) = 0.$$
 (2)

In virtue of (2) the normal magnetic force is found to be, as before,

outside 
$$N_o = 2mxa^{-4}$$
  
inside  $N_i = -mxa^{-4}$ 

so that the apparent surface density  $\sigma = 3mxa^{-4}/4\pi$  is unaltered by the motion.

The magnetic force in the direction of x at r = a is

outside 
$$\alpha_0 = -ma^{-3} + 3mx^2a^{-5} + Cxa^{-5}(a^3\chi''' + a^2\chi'') - Cx^3a^{-7}(a^3\chi''' + a^2\chi'')$$
  
and inside  $\alpha_0 = -ma^{-3}$ .

Thus

$$\frac{1}{2}(\alpha_0 + \alpha_1) = -ma^{-3} + \frac{8}{9}mx^2a^{-5} + \frac{1}{2}Cxa^{-6}(1 - x^2/a^2)(a^3\chi''' + a^2\chi'').$$

. Hence the force in the direction of w due to the magnetic force acting on the apparent surface density is

$$= \frac{1}{2} \int (\alpha_0 + \alpha_i) \, \sigma \, 2\pi a^2 \sin \theta \, d\theta$$

and this reduces to

$$\frac{1}{8}m\mathrm{C}a^{-3}(a\chi^{\prime\prime\prime}+\chi^{\prime\prime}).$$

The force in the direction of x due to the magnetic force on the surface current is

$$\frac{1}{2} \int (v \gamma_o - w \beta_o) 2\pi a^2 \sin \theta d\theta$$

and this reduces to

$$\frac{1}{6} m C a^{-3} (a \chi''' + \chi'').$$

Thus the total force in the direction of x due to radiation

$$= \frac{2}{5}mCa^{-3}(a\chi^{\prime\prime\prime} + \chi^{\prime\prime}).$$

But in a uniformly accelerated motion  $\chi''' = 0$ , and from (2)

$$C\chi'' = -m\ddot{\xi}/C^2$$
$$-\frac{2}{3}m^2a^{-3}C^2\ddot{\xi}.$$

so that the force is

Hence the magnetic inertia of the sphere for uniform acceleration in the direction of its magnetic axis is

$$\frac{2}{5}m^2a^{-3}C^{-2}$$
.

(2) Let the sphere be magnetised parallel to the axis of z. When the sphere is at rest the magnetic forces are given by

inside 
$$(\alpha, \beta, \gamma) = -ma^{-3}(0, 0, 1)$$
  
outside  $(\alpha, \beta, \gamma) = -mr^{-3}(0, 0, 1) + 3mzr^{-5}(x, y, z)$ .

Thus the tangential component of  $(\alpha, \beta, \gamma)$  is continuous at r = a, and the apparent surface density is  $\sigma = 3mza^{-a}/4\pi$ .

Now, let the sphere move under the action of a mechanical force so that the displacement along the axis of x at any time is  $\xi$ . The appropriate forms to be assumed for the forces outside are

$$(\alpha, \beta, \gamma) = -mr^{-3}(0, 0, 1) + 3mzr^{-5}(x, y, z) + Czr^{-5}(1, 0, 0)(r^3\chi''' + 2r^2\chi'' + 3r\chi' + 3\chi + 3\xi m/C) + Cxr^{-5}(0, 0, 1)(r^2\chi'' + 3r\chi' + 3\chi + 3\xi m/C) - Czzr^{-7}(x, y, z)(r^3\chi''' + 6r^2\chi'' + 15r\chi' + 15\chi + 15\xi m/C), (X, Y, Z) = Cr^{-3}(0, 1, 0)(r\chi'' + \chi') - Czr^{-5}(0, z, -y)(r^2\chi''' + 3r\chi'' + 3\chi').$$

Hence

$$(X', Y', Z') = Cr^{-3}(0, 1, 0)(r\chi'' + \chi' + \xi m/C^2)$$

$$- Czr^{-5}(0, z, -y)(r^3\chi''' + 3r\chi'' + 3\chi' + 3\xi m/C^2).$$

Inside we may take

$$(\alpha, \beta, \gamma) = -ma^{-3}(0, 0, 1)$$

and assume currents at the surface r = a, viz.

$$(u, v, w) = Cza^{-6}(0, -z, y) P.$$

Thus the tangential component of X', Y', Z' will vanish at r = a if

$$a\chi'' + \chi' + \xi m/C^2 = 0$$

and

$$a^2\chi''' + 3a\chi'' + 3\chi' + 3\xi m/C^2 = 0.$$

Again the tangential discontinuity of  $\alpha$ ,  $\beta$ ,  $\gamma$  will measure the surface current if

$$4\pi P = -(a^3\chi^{\prime\prime\prime} + 2a^2\chi^{\prime\prime} + 3a\chi^{\prime} + 3\chi + 3\xi m/C)$$
$$3\xi m + C(a^2\chi^{\prime\prime} + 3a\chi^{\prime} + 3\chi) = 0.$$

and

These conditions reduce to two, viz.,

$$4\pi P = -a^2 \chi^{\prime\prime}, \tag{3}$$

$$3\xi m + C(a^2\chi'' + 3a\chi' + 3\chi) = 0, \tag{4}$$

provided  $\gamma^{\prime\prime\prime}=0$ .

Under these conditions the normal component of magnetic force outside reduces to

$$N_o = 2mza^{-4}$$

and inside

$$N_i = -mza^{-4},$$

so that the apparent surface density remains  $\sigma = 3za^{-4}/4\pi$ .

The magnetic force in the direction of x at r = a is

outside 
$$\alpha_0 = 3mzxa^{-5} + Cza^{-5}(1-x^2/a^2)a^2\chi''$$
,

inside 
$$\alpha_i = 0$$
,

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$$\frac{1}{2}(\alpha_0 + \alpha_i) = \frac{3}{4} mzxa^{-5} + \frac{1}{2} Cza^{-5} (1 - x^2/a^2) a^2 \chi''.$$

Thus the force in the direction x due to the magnetic force acting on the apparent surface density is

$$\frac{1}{2}\int\sigma\left(\alpha_{o}+\alpha_{i}\right)a^{2}\sin\theta\,d\theta\,d\phi,$$

which reduces to  $\frac{1}{2}mCa^{-3}\gamma''$ .

$$\frac{3}{8}mCa^{-3}\chi^{\prime\prime}$$
.

The force in the direction x due to the magnetic force acting on the surface current is

$$= \frac{1}{2} \left\{ v \left( \gamma_0 + \gamma_i \right) - w \beta_0 \right\} a^2 \sin \theta \, d\theta \, d\phi,$$

and this reduces to

$$\frac{3}{4}mCa^{-3}\chi^{\prime\prime}$$
.

The total force in the direction of x due to radiation is thus

$$\frac{4}{3}mCa^{-3}\chi^{\prime\prime}$$
.

Hence since  $C\chi'' = -m\ddot{\xi}/C^2$  for a uniformly accelerated motion, the force is

$$-\frac{4}{5}m^2a^{-3}C^{-2}\xi$$
.

Hence the magnetic inertia of the sphere for uniform acceleration at right angles to the axis of magnetisation is

We may now consider some applications of these results.

In the case of the Earth, the electric inertia, assuming a normal potential gradient at the surface of 1 volt per cm., comes to 2·1 grm. The magnetic moment of the Earth is, according to Gauss,  $8\cdot6\times10^{25}$  C.G.S. magnetic units. Thus the magnetic inertia parallel to its magnetic axis works out to  $1\cdot3\times10^4$  grm. Thus the magnetic inertia is more important than the electric inertia, although it is still very small compared with the gravitational inertia, viz.,  $6\times10^{27}$  grm.

The ratio of magnetic to gravitational inertia for the Earth is thus  $2 \times 10^{-24}$ .

Prof. Hale's measurements lead to the conclusion that the surface magnetic forces on the Sun are 100 times those at the Earth's surface, and as its density is but a quarter of that of the Earth, the corresponding ratio for the Sun would be about  $8 \times 10^{-20}$ .

The fact that the inertia along and perpendicular to the magnetic axis are different is of interest. For since the Earth's magnetic axis is inclined to the axis of rotation, and this again is inclined to the plane of the ecliptic, there will be a small diurnal variation of the effective inertia of the Earth, which may be expected to lead to small diurnal corrugations in the Earth's path. It seems, however, doubtful if this effect could be measured within any reasonable astronomical time.

The results are also of interest in the theory of electrons and magnetons. The electronic charge is  $1.7 \times 10^{-20}$  (in electromagnetic units), while the magnetic moment of the magneton is  $1.8 \times 10^{-21}$  (in magnetic units). If we suppose that in each case the radius is  $1.5 \times 10^{-18}$ , we find that the electric inertia is  $1.3 \times 10^{-27}$ , and the magnetic inertia is  $4 \times 10^{-25}$ . Thus the magnetic inertia is more important than the electric inertia.

There are, however, difficulties of a serious nature in supposing that the radius of a magneton is as small as  $1.5 \times 10^{-18}$ , and in these 'Proceedings,' A, vol. 91, p. 156 (1915), I give reasons for thinking that the radius is more nearly  $1.5 \times 10^{-10}$ .

The electric inertia would then be  $1.3 \times 10^{-30}$  and the magnetic inertia  $4 \times 10^{-34}$ .

It may be inferred from the results for the inertia of a magnetic doublet that the like results hold for an electric doublet where m stands for the electric moment in electrostatic units.

An unpolarised body consisting of electric or magnetic doublets may be supposed to have the axes of the doublets orientated equally in all directions. On the average the inertia per doublet is  $\frac{2}{3}m^2a^{-3}C^{-2}$ , and thus there is a contribution to the inertia of such a body of amount  $\frac{3}{4}Nm^2a^{-3}C^{-2}$  per unit volume, where N is the number of doublets per unit volume. We may form an estimate of the order of magnitude of this effect.

I have shown\* that the dielectric constant of a gas is given by

$$K = 1 + 4\pi N m^2 M^{-1} \bar{v}^{-2},$$

where M is the mass of a particle and  $\tilde{v}$  the velocity of mean square. Clearly a similar form would hold for the magnetic permeability if the particles were magnetic doublets.

Boltzmann's value of K-1 for hydrogen is  $26.5 \times 10^{-5}$ , and this with the usual estimates gives the electric moment per molecule (m) about  $3 \times 10^{-19}$  and a about  $6 \times 10^{-10}$ . If these values are applicable to a solid for which N is about  $10^{24}$ , the inertia per unit volume on account of the electric doublets would be of order  $10^{-6}$  or  $10^{-7}$ .

We have then an effect which may prove capable of measurement. It involves a new combination of the molecular quantities and is connected with the magnetic permeability or dielectric constant of the material.

Note.—Sir J. J. Thomson has pointed out to me that the magnetic inertia may be calculated in a simple way by the method which he used in his original calculation of electric inertia for a charged sphere.

I may also add that the rotation of a magnetised sphere may be examined by the method in the paper. I find that for rotation about the magnetic axis the moment of inertia is  $\frac{2}{6}m^2a^{-1}C^{-2}$ , and for rotation about an axis at right angles to the magnetic axis it is  $\frac{4}{5}m^2a^{-1}C^{-2}$ .

\* 'Roy, Soc. Proc.,' A, vol. 69, p. 394.

# The Effective Inertia of Electrified Systems Moving with High Speed.

By GEORGE W. WALKER, A.R.C.Sc., M.A., F.R.S., formerly Fellow of Trinity College, Cambridge.

(Received March 23, 1917.)

The following investigation is supplementary to a paper dealing with the same problem communicated to the Society some years ago.\* In that paper I showed that the method of deducing the inertia of an electrified system, moving with a high constant speed, from consideration of the energy or the electromagnetic momentum of such a steady state was logically incorrect; and I developed a method of dealing with the problem which depends directly on the general electromagnetic equations, and so is free from this objection.

Application of the method to an electrified sphere showed that Sir J. J. Thomson's expression for transverse inertia (using his surface conditions) was correct, but that Abraham's expression (which involves a different surface condition) was not confirmed. Larmor and Lorentz independently showed there is complete correspondence between an electrified system at rest and another system maintained in uniform linear motion, provided the linear scale of the second system is contracted in the ratio  $(1-k^2)^{\frac{1}{2}}$ , where k is the ratio of the speed of the system to that of radiation.

While such a contraction would provide an explanation of the null result of the Michelson-Morley experiment, no proof has ever been given that a specified system at rest will, when set in uniform motion, actually undergo precisely this contraction. This assumption is, however, tacitly made in Einstein's theory of "relativity," and is in fact an essential feature of that theory.

Lorentz suggested that an electron, supposed spherical at slow speeds, might undergo the contraction referred to; and, using the electromagnetic momentum of this steady state, he deduced that the electric inertia for longitudinal acceleration would be  $m_0 (1-k^2)^{-3/2}$  and for transverse acceleration  $m_0 (1-k^2)^{-1}$ , where  $m_0$  or  $\frac{3}{3}e^2\alpha^{-1}C^{-2}$  is the inertia for slow speeds.† Precisely the same results are obtained by the "relativity" theory.

These formulæ have been used in discussing experiments on  $\beta$ -rays by Kaufmann, Bucherer, Bestelmeyer, and others, with results that are claimed to prove the correctness of the formula.

<sup>\* &#</sup>x27;Phil. Trans.,' A, vol. 210, pp. 145-197.

<sup>†</sup> See Lorentz, 'Theory of Electrons.'

In view of the objection that I have already raised to the quasi-stationary method of calculating the inertia (admitted by Lorentz), I have for some time wished to apply the more correct method (loc. cit. ante) to the case of a "contracted" electron. We shall consider the electron to have a charge e in electrostatic units distributed on its surface which is of the form

$$(1-k^2)^{-1}x^2+y^2+z^2=a^2$$

when the electron moves in the direction of x with uniform speed kC, where C is the velocity of radiation.

In the steady state of motion of a conductor it is shown by Larmor ('Æther and Matter') that the field referred to an origin moving with the conductor is given by the magnetic force

$$(\alpha, \beta, \gamma) = 0, -k\partial\psi_0/\partial z, k\partial\psi_0/\partial y,$$

and the æthereal electric force

$$(X, Y, Z) = -(1-k^2) \frac{\partial \psi_0}{\partial x}, \quad -\frac{\partial \psi_0}{\partial y}, \quad -\frac{\partial \psi_0}{\partial z},$$

where  $\psi_0$  satisfies

$$(1 - \lambda^2) \frac{\partial^2 \psi_0}{\partial z^2} + \frac{\partial^2 \psi_0}{\partial z^2} + \frac{\partial^2 \psi_0}{\partial z^2} + \frac{\partial^2 \psi_0}{\partial z^2} = 0,$$

and is constant throughout the conductor.

The surface density of electricity is given by

$$4\pi\sigma$$
 = Normal component of  $(X, Y, Z)$ 

and the force effective in moving electricity (called by Larmor the electric force) is

P, Q, R = 
$$-(1-k^2)(\partial \psi_0/\partial x, \partial \psi_0/\partial y, \partial \psi_0/\partial z)$$
.

In the present case we take outside the electron

$$\psi_0 = A\rho^{-1}$$
 where  $A = c(1-k^2)^{-\frac{1}{2}}$   
 $\rho^2 = (1-k^2)^{-1}x^2 + y^2 + z^4$ .

and

while inside  $\psi_0$  is constant.

Thus the conditions are secured and  $\sigma = Apa^{-3}/4\pi$ , where p is the perpendicular on the tangent plane and the total charge is e.

When the system undergoes acceleration from this state of motion with velocity kC, so that the displacement f due to the acceleration is small, the method consists in finding the modified solution of the primary equations of the field true up to first powers of f and its derivatives, and then calculating the reaction. It might be thought that the solution would fail as time progresses and the velocity gradually increases, but this is not really so, for we may start with any value of the velocity kC and thus our solution retains its form at every stage of the motion if we remember that the proper value of the speed is introduced after any differentiations have been performed.

Suppose, then, that the system undergoes linear acceleration in the direction of x, so that the displacement at any time is  $f = \frac{1}{4}\mu t^2$ . The equations for the state of the æther outside are given in my former paper, p. 161, but the equations have to be solved in the present case, subject to the conditions that the tangential component of P, Q, R is zero at the surface  $(1-k^2)^{-1}x^2 + y^2 + z^2 = a^2$ , and that the interior is free from electric and magnetic force.

Using the same notation as before, we find that the solution is expressed as follows:—

Let 
$$\phi = (Ct - \lambda x)^2 \phi_1 + (Ct - \lambda x) \phi_2 + \phi_3,$$
 subject to 
$$(\partial/\partial t - k\partial/\partial x)^2 \phi = C^2 \nabla^2 \phi,$$
 where 
$$\lambda = k (1 - k^2)^{-1},$$
 then 
$$\phi_1 = B\rho^{-1}, \quad \phi_2 = Dx\rho^{-3}, \quad \phi_3 = B(1 - k^2)^{-1}\rho^{-1},$$
 where 
$$B = \frac{1}{2}\mu A C^{-2}, \quad D = \frac{2}{3}\lambda Ba^2,$$
 also 
$$\chi = Ex \rho^{-3} + Fx\rho^{-6} \{3 - 5(1 - k^2)^{-1}x^2\rho^{-2}\},$$
 where 
$$E = \frac{1}{3}(5 - 3k^2)(1 - k^2)^{-2}Ba^2$$
 and 
$$F = \frac{1}{3}k^2(1 - k^2)^{-2}Ba^4.$$

We may thus verify that at the surface of the electron the æthereal electric force is given by

$$(X, Y, Z) = Aa^{-3}(x, y, z) - 4BCt\lambda xa^{-3}(1, 0, 0)$$

$$+ 4BCtk(1 - k^{3})^{-2}x^{2}a^{-5}(x, y, z)$$

$$- 4B(1 - \frac{1}{5}k^{2})(1 - k^{3})^{-2}xa^{-3}(x, y, z),$$

$$P = X.$$

while

Thus the surface density of electricity is given by

$$4\pi\sigma = Apa^{-3} - 4B(1 - \frac{1}{4}k^2)(1 - k^2)^{-2}xpa^{-3}$$

where p is perpendicular on the tangent plane.

Hence the force on the electron in the direction of x

$$= \frac{1}{2} \int \sigma \mathbf{P} d\mathbf{S}.$$

Neglecting squares of  $\mu$  (the acceleration), as we have done consistently, the force reduces to

$$-\frac{1}{2}$$
 A . B  $(1-\frac{1}{6}k^2)(1-k^2)^{-2}a^{-6}\int px^2dS$ .

The value of the integral is readily found to be

$$\frac{1}{8}4\pi a^{5}(1-k^{2})^{N/2}$$
.

Substituting the values of A and B, we find that the force due to the æther reaction is

$$-\frac{3}{5}e^{2}(1-\frac{1}{5}k^{2})(1-k^{2})^{-3/2}a^{-1}C^{-2}\mu$$

and thus the inertia for longitudinal acceleration is

$$\frac{2}{3}e^2a^{-1}C^{-2}(1-\frac{1}{3}k^2)(1-k^2)^{-3/2}$$

When acceleration in the direction of y is imposed we may again take  $f = \frac{1}{2} \mu t^2$  and the general equations to be solved are those of my former paper, p. 166. (Note a misprint. In the expression for  $\gamma$  there should be a term  $\frac{1}{C} \frac{\partial^2 \phi}{\partial t \partial x}$  in place of  $\frac{1}{C} \frac{\partial^2 \phi}{\partial t \partial z}$ ).

The condition is, again, that the tangential component of P, Q, R should vanish at the surface of the electron, and that the interior should be free from force.

The value of  $\phi$  is exactly the same as that required for longitudinal acceleration, but the value of  $\chi$  is now

$$\chi = Ey\rho^{-3} + Fy\rho^{-5} \{1 - 5(1 - k^2)^{-1}x^2\rho^{-2}\}$$

where

$$E = (1 - \frac{1}{k}k^2)(1 - k^2)^{-1} Ba^2$$

and

$$\mathbf{F} = \frac{1}{3} k^2 (1 - k^2)^{-1} Ba^4.$$

We find that at the surface of the electron

$$Q = (1 - k^{2}) Aya^{-3} + 4kCt Bxy^{2}a^{-5} - 4B (1 + \frac{1}{10}k^{2}) y^{2}a^{-3}$$

$$(X, Y, Z) = Aa^{-3}(x, y, z) - \frac{2}{3}Ba^{-1}k^{2}(1 - k^{2})^{-1}(0, 1, 0)$$

$$-2kCt Ba^{-3}(y, (1 - k^{2})^{-1}x, 0) + 4kCt B (1 - k^{2})^{-1}a^{-5}xy(x, y, z)$$

$$-4B(1 + \frac{1}{10}k^{2})(1 - k^{2})^{-1}a^{-3}y(x, y, z).$$

The surface density is given by  $\sigma$ , where

$$4\pi\sigma = \mathrm{A}pa^{-3} - 4\mathrm{B}\left(1 + \frac{1}{10}k^2\right)(1 - k^2)^{-1}ypa^{-3} - \frac{9}{3}\mathrm{B}k^2(1 - k^2)^{-1}ypa^{-3}.$$

The force in the direction of y is

and neglecting squares of the acceleration this reduces to

$$-\frac{1}{\pi} AB (1 + \frac{1}{66} k^2) a^{-6} \int py^2 dS.$$

The integral is

$$= \frac{1}{4} 4\pi a^5 (1-k^2)^{\frac{1}{2}},$$

so that the force due to the æther reaction is

$$-\frac{2}{3}e^{2}(1+\frac{1}{86}k^{2})(1-k^{2})^{-\frac{1}{2}}a^{-1}C^{-2}\mu$$

and the inertia for transverse acceleration is

$$\frac{2}{3}e^2a^{-1}C^{-2}(1+\frac{1}{60}k^2)(1-k^2)^{-\frac{1}{6}}$$

Thus, the results obtained by Lorentz' method and by the relativity theory are not confirmed for a contracted electron of the type of a conductor with a surface charge, so that, unless some arithmetical error has occurred, the difference found is vital in the application to the experiments on the deflection of  $\beta$ -rays.

An objection to the preceding calculation may be raised. It might be argued that I ought to have supposed that the contracted electron should alter in shape as the acceleration proceeds. But the difficulty is to know how it alters. There is no correspondence between accelerated motions at different speeds such as can be proved for uniform speeds, for the transformation entirely breaks down if the velocity is not constant. One might, as a pure hypothesis which has no a priori justification, assume that the surface is deformed according to the same law as holds for uniform velocity. This could be worked out, and might lead to a first-order term (in acceleration) for longitudinal inertia, but clearly would lead to only second-order terms for transverse inertia. But this appears to me too speculative to be of any value at present.

Experimental researches on the inertia of electrons have been made by Kaufmann,\* Bestelmeyer,† Bucherer,‡ and Wolz,§.

In my former paper I have shown that J. J. Thomson's expression for the electric inertia agrees very well with Kaufmann's numbers. Using the same method of analysing the observations as formerly, I find the new expression for transverse inertia, viz.,  $m_0(1+\frac{1}{60}k^2)(1-k^2)^{-\frac{1}{2}}$ , agrees equally well. I should have given this calculation but for the fact that, when Bucherer's numbers were examined, they would not stand such a severe test, and the method of least squares had to be used to give them a reasonable chance. Hence, for comparison, I have treated Kaufmann's numbers also by least squares.

The following Table is based on the Table (loc. cit., p. 170) which was originally prepared from Kaufmann's paper. I have simplified it by calculating  $\mu/e$ , where  $\mu$  is the effective mass  $m+m_0f(k)$  and  $f(k)=(1+\frac{1}{6}\frac{1}{6}k^2)(1-k^2)^{-\frac{1}{6}}$ .

<sup>\* &#</sup>x27;Gött. Nachrichten,' 1903, Heft 3.

<sup>† &#</sup>x27;Ann. d. Phys.,' vol. 22, p. 440 (1907).

<sup>† &#</sup>x27;Ann. d. Phys.,' vol. 28, p. 513 (1909).

<sup>§ &#</sup>x27;Ann. d. Phys.,' vol. 30 (1909).

k.	Observed $\mu/e \times 10^{-8}$ .	f(k).	Calculated, $\mu/e \times 10^{-8}$ .	O-C.
0 .936	12 .047	8 ·297	12 013	+0.084
0 .866	9 . 362	2 .278	9 .364	-0.002
0.824	8 643	1 .985	8.619	+0.024
0.786	8 · 109	1 .801	8 · 148	-0.084
0.747	7 .727	1 .658	7 .778	-0.046
0.708	7 498	1 .541	7 .471	+0.022

The formula is

$$10^8\mu/e = 3.484 + 2.587 f(k)$$

and hence

$$e/\mu = 1.647 \times 10^7 \times \frac{6.071}{[3.484 + 2.587 f(k)]}$$

I need hardly say that the computation is carried further than the experiments really warrant, for Kaufmann's original curve was only 5 mm. long, and the electric deflection for the largest value of k only 0.6 mm.

The next Table is prepared from Bestelmeyer's values.

k.	Observed, $\mu/e \times 10^{-8}$ .	f(k).	Calculated, $\mu/e \times 10^{-8}$ .
0 ·195	5 .893	1 .026	5 -893
0 .247	5 .959	1 .043	5 .959
0.322	6.086	1 .076	8.086

The formula is

$$10^8\mu/e = 1.933 + 3.860 f(k)$$

and hence

$$e/\mu = 1.726 \times 10^7 \times \frac{5.793}{[1.933 + 3.860 f(k)]}$$

The observed and calculated values are identical, but equally good agreement would be obtained by Thomson's or Lorentz' formula.

The following is prepared from Bucherer's values:-

	1 . 10=9	(1)	Lorentz	Calcu	lated.	Present,	Lorentz
k.	μ/e × 10 <sup>-8</sup> .	f (k).	form.	Present.	Lorentz.	O-C.	0-C.
0 ·817 0 ·879 0 ·428 0 ·515 0 ·687	6 :284 6 :844 6 :508 6 :811 8 :092	1 '074 1 '109 1 '144 1 '228 1 '495	1 ·054 1 ·081 1 ·106 1 ·166 1 ·376	6 ·197 6 ·353 6 ·509 6 ·860 8 ·071	6 ·217 6 ·869 6 ·511 6 ·851 8 ·039	+ 0 ·087 - 0 ·009 - 0 ·001 - 0 ·049 + 0 ·021	+0.017 -0.025 -0.003 -0.040 +0.058

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The present formula gives

$$10^{8}\mu/e = 1.418 + 4.45 f(k) .$$

$$e/\mu = 1.704 \times 10^{7} \times \frac{5.868}{[1.418 + 4.45 f(k)]}.$$

while Lorentz' gives

or

or 
$$\begin{aligned} 10^8 \mu/e &= 0.251 + 5.66 \, f(k) \\ e/\mu &= 1.692 \times 10^7 \times \frac{5.911}{\left[0.251 + 5.66 \, (1 - k^2)^{-\frac{1}{2}}\right]}. \end{aligned}$$

There is a slight advantage in favour of the corrected formula, but these observations are not nearly so consistent as Kaufmann's or Bestelmeyer's. Moreover, the Table does not reveal the serious internal discrepancies in Bucherer's numbers. When taken in pairs, they give great variations in the coefficient of f(k). A considerable discussion took place between Bestelmeyer and Bucherer as to the accuracy of the latter's work, into which I do not propose to enter, but it leaves some doubt about the value of the investigation. Wolz, working under Bucherer's direction, repeated some of his work, with similar results.

My attention has recently been called to a recent paper on "Cathode Rays" by Guye and Lavanchy.\* They compare their experiments over a range of speed from one quarter to one half the speed of light with Abraham's formula and Lorentz' formula. There is greatly superior agreement with Lorentz' formula.

I should have liked to analyse their data by means of the corrected formula for a contracted electron, but, unfortunately, they do not give the original measurements, and the values of speed and inertia can only be deduced from these by means of the formula it is desired to test. But the numbers they give for the Lorentz-Einstein formula are readily found to be in equally good agreement with the formula I have obtained when a small proportion of ordinary inertia is assumed.

From the experiments as a whole, it appears to me very difficult to maintain that they afford a conclusive proof that the Lorentz-Einstein formula is correct, and hence that the inertia is wholly electromagnetic, and that the electron is contracted in the ratio  $(1-k^2)^{\frac{1}{2}}$ .

On the experimental side it is found that J. J. Thomson's formula, or the corrected formula proved for a contracted electron, agrees equally well with observation, but assigns a proportion of ordinary inertia. The experiments are, in fact, inadequate to distinguish between a number of formulæ that might be proposed.

<sup>\* &#</sup>x27;Arch. des Scionces,' Geneva, 1916.

On the theoretical side I have shown that J. J. Thomson's formula is confirmed by the present method of analysis, and that the Lorentz-Einstein formula for a "contracted" electron requires to be modified in the manner stated.

If it be argued, as may fairly be done, that the experiments do not conflict with the Lorentz-Einstein formula, we require to give up the view that the electron is contracted in the proportion they assume. But it is fairly certain that there is an electron of form intermediate between Abraham's sphere and Lorentz' spheroid which would have a transverse inertia correctly given by  $m_0$   $(1-k^2)^{-\frac{1}{2}}$ . This, however, implies giving up the correspondence assumed in the relativity theory, and we might choose between this and the alternative view (by no means unreasonable) that electrons as obtained in experiments possess ordinary as well as electric inertia.

It appears that still further experiments are required, and it would be helpful if results were represented in a form that could be used to test any formula and not any particular one. The subject is still too uncertain to warrant the view that any special formula represents the end of the matter.

On the Mode of Approach to Zero of the Coefficients of a Fourier Series.

By W. H. Young, F.R.S.

(Received February 2, 1917.)

§ 1. In the present communication I give a number of results on the mode of approach to zero of the coefficients of a Fourier series, to which I have already made allusion in my paper on "The Order of Magnitude of the Coefficients of a Fourier Series." These results are not merely curious, they have a real importance, and give one an insight into the nature of these series, which cannot easily be gained without them. Indeed, while the earlier paper leads, as I showed in a subsequent communication, to the discovery of classes of derived series of Fourier series, which, although not themselves Fourier series, none the less converge, and are utilisable in a similar manner, and is therefore in a certain sense of practical interest, the present paper does something towards the elucidation of the general theory of the convergence of Fourier series themselves, as well as of their derived series.

It will be sufficient to give a single instance. I have recently shown that vol. xciii.—A. 2 N

the well-known test of Dirichlet for the convergence of a Fourier series admits of a remarkable generalisation. It follows from Theorem 1, given below (§ 7), that the convergence secured by that test and by its generalisation alike possess what may be called greater strength than the rival tests of Dini and de la Vallée Poussin.

§ 2. In the course of the proofs of the auxiliary theorems A1, ..., we shall require the following Lemmas:

**LEMMA** 1.—The expression  $(x+1)^p-x^p$  is  $\leq 0$  according as  $p \leq 0$ , and is monotone descending or ascending with respect to x according as  $p \le 1$ .

**LEMMA** 2.—For all values of p > 1, the expression  $(x+1)^p - 2x^p + (x-1)^p$  is positive, and it decreases or increases with respect to x according as  $p \leq 2$ .

**LEMMA** 3.—If 
$$p_1 > p_2 > p_3 > ... > p_n > 0$$
, then

$$|p_1u_1 + p_2u_2 + ... + p_nu_n| \le p_1 \times max. \ value \ of \ (u_1 + u_2 + ... + u_r), \ for \ 1 \le r \le n.$$

Also if 
$$0 < p_1 < p_2 < p_3 < ... < p_n$$
, then

$$|p_1u_1 + p_2u_2 + ... + p_nu_n| \le 2p_n \times max$$
, value of  $(u_1 + u_2 + ... + u_r)$ , for  $1 \le r \le n$ .

**Lemma 4.**—If 
$$S_r = \frac{1}{2} + \sum_{r=1}^{r} \cos sx$$
, or if  $S_r = -\frac{1}{2} \cot \frac{1}{2}x + \sum_{r=1}^{r} \sin sx$ , then

$$|S_r| \leq \frac{1}{2} |\operatorname{cosec} \frac{1}{2} x|;$$

and if 
$$T_r = \sum_{i=1}^{r} S_i$$
, then  $|T_r| \le \frac{1}{2} \csc^2 \frac{1}{2} x$ 

$$|T_r| \leq \frac{1}{2} \operatorname{cosec}^2 \frac{1}{2} x$$
.

§ 3. THEOREM A1.—If  $0 , and <math>0 < v \le e$ , where  $e \le \pi$ , then either of the expressions

$$(nv)^{p} \left\{ \sum_{r=2}^{n-1} \left( \sin rv - \frac{\sin}{\cos} (r-1) v \right) (1-r/n)^{p} - (1-1/n) \frac{\sin}{\cos} v \right\}$$

is a bounded function of (v, n),

The argument being the same in both cases, we only treat the sine expression, which we shall denote by S.

. Let us consider separately the values of  $nv \leq B$  and those > B, where B is any fixed positive quantity.

In the former case,

$$|S| = \left| v^p \sum_{r=1}^{n-1} \sin rv \left[ (n-r)^p - (n-r-1)^p \right] \right| \le v^p \sum_{r=1}^{n-1} \left[ (n-r)^p - (n-r-1)^p \right] \le B^p,$$
 so that S is bounded.

In the latter case, v > B/n, and we have

$$S = v^{p} \sum_{r=1}^{n-1} \sin rv \left[ (n-r)^{p} - (n-r-1)^{p} \right] = v^{p} \sum_{r=1}^{n-1} \sin (n-r) v \left[ r^{p} - (r-1)^{p} \right]$$
$$= v^{p} \sum_{r=1}^{n-1} (\sin nv \cos rv - \cos nv \sin rv) \left[ r^{p} - (r-1)^{p} \right].$$

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Hence 
$$|S| \le |L_p| + |M_p|$$
 (1)

where 
$$L_p = v^p \sum_{r=1}^{n-1} \cos rv [r^p - (r-1)^p],$$
 (2)

and  $M_p$  only differs from  $L_p$  in having sines in place of the cosines.

Let us divide the interval (0, nv) into n equal parts; each of these is, by hypothesis, less than e, and the point B will lie in one of them, or coincide with one of the points of division. Denoting this part as the (s+1)-th, we have therefore.

$$sv \le B < (s+1) v < B + e. \tag{3}$$

Divide the summation  $L_p$  into two parts at the s-th term. Writing  $L_{p,1}$  and  $L_{p,2}$  for the two parts, we have

$$|L_{p,1}| = |v^{p} \sum_{r=1}^{s-1} \cos rv [r^{p} - (r-1)^{p}]| \le v^{p} \sum_{s=1}^{s-1} [r^{p} - (r-1)^{p}] \le v^{p} s^{p} \le B^{p}.$$
 (4)

Also, using our Lemmas 1, 3 and 4,

$$|L_{p,2}| \le v^p \left[ (s+1)^p - s^p \right] \times \text{max. value of } \sum_{r=s+1}^k \cos rv, \qquad (s+1 \le k \le n-1),$$

$$\le v^p \left[ (s+1)^p - s^p \right] \operatorname{cosec} \frac{1}{2}v \le 2B^{p-1} p \left( \frac{1}{2}e \operatorname{cosec} \frac{1}{2}e \right), \tag{5}$$

since  $\frac{1}{4}v$  cosec  $\frac{1}{4}v$  is a monotone increasing function of v from 0 to  $\pi$ .

Thus,  $L_{p,1}$  and  $L_{p,2}$  being bounded,  $L_p$  is bounded, and similarly  $M_p$  is bounded, therefore, by (1), S is bounded, which proves the theorem.

§ 4. Theorem A2.—If 1 < p and  $0 < v \le e$ , where  $e \le \pi$ , then either of the expressions

$$nv \left\{ \sum_{r=2}^{n-1} \binom{\sin rv - \sin (r-1)v}{\cos (r-1)v} (1-r/n)^p - (1-1/n) \frac{\sin v}{\cos v} \right\}$$

is a bounded function of (v, n).

This theorem may be most easily proved by the same method as that used in the preceding article, bearing in mind that, since p is now greater than unity,  $\{r^p-(r-1)^p\}$  is positive and monotone increasing. We prefer, however, to give the following method, as it involves certain expressions required in the sequel. The equations (1)—(4) of the preceding article still hold. We then proceed as follows:—

$$L_{p,3} = v^p \sum_{r=s+1}^{n-1} (S_r - S_{r-1}) [r^p - (r-1)^p]$$

$$= v^p \{ S_s [(s+1)^p - s^p] - \sum_{s=s+1}^{n-1} S_r [(r+1)^p + (r-1)^p - 2r^p] + S_{n-1} [(n-1)^p - (n-2)^p] \},$$
(6)

where  $S_r = \frac{1}{2} + \cos v + \cos 2v + \dots + \cos rv$ .

By Lemma 2, the expression  $[(r+1)^p+(r-1)^p-2r^p]$  is positive and monotone decreasing, if  $1 . Hence, by Lemmas 3 and 4, the corresponding summation which occurs in the expression for <math>L_{p,2}$  is numerically less than

$$\csc^2 \frac{1}{2} v \left[ (s+1)^p + (s-1)^p - 2s^p \right]$$

$$= s^{p-2} p(p-1) \csc^2 v \left\{ \frac{(s+1)^p + (s-1)^p - 2s^p}{p(p-1) s^{p-2}} \right\} \le s^{p-2} p(p-1) \csc^2 v.$$

This has to be multiplied by  $v^p$ , and is therefore evidently bounded, since, by (3) of the preceding article,  $(vs)^{p-2}$  is bounded.

Also, as in the discussion of (5) of the preceding article,

$$v^p \mathbf{S}_s \left[ (s+1)^p - s^p \right] \leq 2 \mathbf{B}^{p-1} p \left( \tfrac{1}{2} e \operatorname{cosec} \, \tfrac{1}{2} e \right),$$

so that this is also bounded. Thus

$$L = 0(1) + v^{p} S_{n-1} [(n-1)^{p} - (n-2)^{p}], \qquad (1$$

which is the expression above referred to as required in the sequel and leads to our present theorem, since by Lemma 4,  $vS_{n-1}$  is bounded, so that

$$\mathbf{L}_{p} = 0 \, (nv)^{p-1}.$$

A similar result holding for M, it follows, as in the preceding article, that  $(nv)^{-p+1}S$ , which is the expression given in the enunciation of the present theorem, is bounded. This proves the theorem, when 1 .

If  $2 \le p$ , we still have (6); but now  $\{(r+1)^p + (r-1)^p - 3r^p\}$  is monotone increasing; the term with the summation on the right of (6) is therefore numerically less than

$$v^p 2 \csc^2 \frac{1}{2} v \left[ (n+1)^p + (n-1)^p - 2n^p \right] = 0 (nv)^{p-2},$$

since, writing x in the place of  $n^{-1}$ , we have by indeterminate forms,

Lt 
$$n^{-p+2}[(n+1)^p + (n-1)^p - 2n^p]$$
  
= Lt  $x^{-2}[(1+x)^p + (1-x)^p - 2] = p(p-1)$ .

Instead of (7), we have now

$$L_p = 0 (nv)^{p-2} + v^p S_{n-1} [(n-1)^p - (n-2)^p)], \qquad (2 \le p), \tag{7'}$$

whence our result follows as before.

§ 5. Theorem B1.—If  $0 , and <math>0 < v \le e$ , where  $e \le \pi$ , then either of the expressions

$$(nv)^{p} \sum_{r=1}^{n-1} n^{-1} \left\{ r \sin_{cos} rv - (r-1) \sin_{cos} (r-1) v \right\} (1-r/n)^{p}$$

is a bounded function of (v, n).

It is only necessary to discuss the sine expression.

If nv < B, the expression is clearly bounded. For, denoting it by T, we have, since  $(1-r/n)^p$  is monotone descending,

$$|T| \le \frac{1}{n} (1-1/n)^p \times \text{max. value of } \sum_{r=1}^k [r \sin rv - (r-1) \sin (r-1)v]$$
  
  $\le (1+1/n) (1-1/n)^p.$ 

If B = nv, we have

$$T = v^{p} \sum_{r=1}^{n-1} \frac{r}{n} [(n-r)^{p} - (n-r-1)^{p}] \sin rv$$

$$= v^{p} \sum_{r=1}^{n-1} (1-r/n) [r^{p} - (r-1)^{p}] \sin (n-r) v = P_{1} \sin nv - P_{2} \cos nv, \quad (1)$$

where

$$P_{1} = v^{p} \sum_{r=1}^{n-1} (1 - r/n) [r^{p} - (r-1)^{p}] \cos rv$$

$$= v^{p} \sum_{r=1}^{n-1} \{ [r^{p} - (r-1)^{p}] - n^{-1} [(r^{p+1} - (r-1)^{p+1} + (r-1)^{p}] \} \cos rv$$

$$= L_{p} - (nv)^{-1} L_{p+1} + n^{-1} M_{p}, \qquad (2)$$

where  $L_p$  has the same meaning as in the preceding articles,  $L_{p+1}$  being the same, with (p+1) in place of p, and

$$M_p = v^p \sum_{r=1}^{n-1} (r-1)^p \cos rv.$$
 (3)

If p < 1,  $L_p$  is bounded by Theorem A1, and by Theorem A2  $L_{p+1}$  is of the order  $0 (nv)^p$ . Also since  $(r-1)^p$  is positive and monotone increasing,

$$\left| n^{-1} \mathbf{M}_{p} \right| \leq n^{-1} v^{p} \, 2(n-2)^{p} \, \operatorname{cosec} \, \tfrac{1}{2} v \quad (nv)^{p-1} \, 4(\tfrac{1}{2} v \, \operatorname{cosec} \, \tfrac{1}{2} v) \leq \mathbf{B}^{p-1} \, 2e \, \operatorname{cosec} \, \tfrac{1}{2} e.$$

Thus  $P_1$  is bounded. Similarly  $P_2$  is bounded, and therefore, by (1), the required result follows, when 0 .

If  $1 \le p < 2$ , we have, using the expressions (7) and (7'), found in § 4,

$$L_p = 0(1) + v^p S_{n-1} [(n-1)^p - (n-2)^p],$$

$$(nv)^{-1} \mathbf{L}_{p+1} = 0 (nv)^{p-2} + v^p \mathbf{S}_{n-1} n^{-1} [(n-1)^{p+1} - (n-2)^{p+1}].$$

Also

$$\mathbf{M}_{p} = v^{p} \sum_{r=1}^{n-1} (\mathbf{S}_{r} - \mathbf{S}_{r-1})(r-1)^{p} = v^{p} \sum_{r=1}^{n-2} \mathbf{S}_{r} \left\{ (r-1)^{p} - r^{p} \right\} + v^{p} \mathbf{S}_{n-1} (n-2)^{p}.$$

Since  $[r^p-(r-1)^p]$  is positive and monotone ascending, the summation here is numerically less than

$$2\operatorname{cosec}^2\tfrac{1}{2}v[n^p-(n-1)^p]=8v^{-2}(\tfrac{1}{2}e\operatorname{cosec}\tfrac{1}{2}e)^2pn^{p-1}\Big(\frac{1-(1-1/n)^p}{p/n}\Big),$$

where the last factor on the right  $\rightarrow 1$ , when  $n \rightarrow \infty$ . Since then

$$(nv)^{p-2} < B^{p-2}, \qquad n^{-1}M_p = 0(1) + v^p S_{n-1}n^{-1}(n-2)^p.$$

Hence

$$P_{1} = L_{p} - (nv)^{-1} L_{p+1} + n^{-1} M_{p} = 0 \ (1) + v^{p} S_{n-1} n^{-1} [(n-1)^{p} - (n-2)^{p}]$$
$$= 0 \ (1) + v \ (v S_{n-1}) (nv)^{p-2} p \left( \frac{1 - [1 - 1/(n-1)]^{p}}{p/(n-1)} \right) = 0 \ (1).$$

Thus  $P_1$  is again bounded, whence as before the required result follows, when  $1 \le p < 2$ . This completes the proof of the theorem.

§ 6. The same method, using only the formula (7') and not (7), gives us the theorem:—

THEOREM B2.—If  $2 \le p$ , and  $0 \le v \le c$ , where  $e \le \pi$ , then either of the expressions

$$(nv)^{-2}\sum_{r=1}^{n-1}n^{-1}\left\{r\frac{\sin rv-(r-1)}{\cos}(r-1)v\right\}(1-r/n)^{p}$$

is bounded.

We foresee now the general theorem :-

THEOREM.—If  $0 , and <math>0 < v \le e$ , where  $e \le \pi$ , then either of the expressions

$$(nv)^{p} \sum_{r=1}^{n-1} n^{-q} \left\{ r^{q} \frac{\sin}{\cos} rv - (r-1) \frac{\sin}{\cos} (r-1) v \right\} (1 - r/n)^{p}$$

is bounded. And if  $q+1 \le p$ , the same is true when we change the index p in  $(nv)^p$  into q+1.

The proof of this theorem may be left to the student.

§ 7. We now pass to the main theorems of the paper.

THEOREM 1.—If  $a_n$  is the typical coefficient of the Fourier cosine series of an even function which is such that

(i) 
$$x^{-1} \int_0^x \left| d\{xf(x)\} \right|$$
 is a bounded function of x in the whole interval of periodicity, and

(ii) 
$$x^{-1} \int_0^x f(x) dx$$
 has a unique finite limit  $\beta$  as  $x \to 0$ ,

then 
$$(Ck)(na_n) \to 0$$
, when  $n \to \infty$ ,  $(0 < k < 1)$ .

We have

$$\frac{1}{2}\pi (Ck) (na_n) = \int_0^{\pi} \sum_{r=1}^{n-1} [r\cos rv - (r-1)\cos (r-1)v] (1-r/n)^k f(v) dv$$

$$= \int_0^{\pi} \psi'_n(v) f(v) dv$$

where 
$$\psi_n(v) = \sum_{r=1}^{n-1} [\sin rv - \sin (r-1)v] (1-r/n)^k$$
.

Thus, by Theorem A1,  $(nv)^k \psi_n(v)$  is bounded for all positive values of v. Let us consider first the part of the integral due to the interval  $(B/n, \pi)$ , where B is a large positive quantity, independent of n, and let us only consider values of n greater than  $B/\pi$ . Let the integral in this interval be denoted by  $I_1$ , and in the remaining interval by  $I_2$ . We have then

$$I_1 = \int_{B/n}^{\pi} \psi'_n(v) f(v) dv = \int_{B/n}^{\pi} v^{-1} \psi'_n(v) v f(v) dv.$$

Now in the interval  $(-\pi, \pi)$  the expression vf(v) is a function of bounded variation, for its total variation is  $2\int_0^\pi \left| d[vf(v)] \right|$ , which by (i) is finite. Let us denote this function of bounded variation by g(v). Then by (i),  $\left| x^{-1}g(x) \right| \leq x^{-1}\int_0^x \left| dg(x) \right| < A'$ , where A' is independent of B and n, we may therefore write

$$I_{1} = \int_{B/n}^{\pi} \phi'_{n}(v) g(v) dv = \left[ \phi_{n}(v) g(v) \right]_{B/n}^{\pi} - \int_{B/n}^{\pi} \phi_{n}(v) dg(v),$$
where
$$\phi_{n}(v) \leq v^{-1} \psi_{n}(v) + \int_{\pi}^{\pi} v^{-2} \psi_{n}(v) dv.$$

It follows at once that  $(nv)^k v \phi_n(v)$  is a bounded function, say numerically less than A, where A is independent of B and n.

We have, therefore, denoting  $\int_{0}^{v} \left| dg(v) \right|$  by G(v),

$$\left| \begin{array}{c} \mathbf{I}_{1} \end{array} \right| \leq \left| \left[ \phi_{n} \left( v \right) g \left( v \right) \right]_{\mathbf{B}/n}^{\pi} \right| + \int_{\mathbf{B}/n}^{\pi} \left| \phi_{n} \left( v \right) \right| d\mathbf{G} \left( v \right) \\ \leq \mathbf{A} \mathbf{A}' \left\{ \left( n \pi \right)^{-k} + \mathbf{B}^{-k} \right\} + \int_{\mathbf{B}/n}^{\pi} \mathbf{A} \left( n v \right)^{-k} v^{-1} d\mathbf{G} \left( v \right). \end{array}$$

Using integration by parts for the evaluation of the last integral, this gives

$$| I_1 | \leq AA' \{ (n\pi)^{-k} + B^{-k} \} + A [ (nv)^{-k} v^{-1} G(v) ]_{B/n}^{\pi}$$

$$+ A(k+1) \int_{B/n}^{\pi} (nv)^{-k} v^{-2} G(v) dv$$

$$\leq 2AA' [ (n\pi)^{-k} + B^{-k} ]$$

$$+ AA' (1 + 1/k) \int_{B/n}^{\pi} d(nv)^{-k} \le AA' (3 + 1/k) [(n\pi)^{-k} + B^{-k}].$$

Hence

$$Lt_{n\to\infty} |I_1| \le AA' (3+1/k) B^{-k},$$

which is as small as we please, B being chosen sufficiently large.

Next, changing the variable to t = nv, and writing  $\chi_n(t) = n^{-1} \psi_{n'}(t/n)$ , we have

$$I_{2} = \int_{0}^{B/n} \psi'_{n}(v) f(v) dv = \int_{0}^{B} \chi_{n}(t) f(t/n) dt$$

$$= \left[ n \chi_{n}(t) \mathbf{F}(t/n) \right]_{0}^{B} - \int_{0}^{B} n t^{-1} \mathbf{F}(t/n) t \frac{d}{dt} \chi_{n}(t) dt.$$

Now  $t \frac{d}{dt} \chi_n(t)$  is easily seen to be a bounded function of  $(t, n)^*$ , and, as  $n \to \infty$ , it approaches  $t \frac{d}{dt} \lambda(t)$ , where

$$\begin{split} \text{Lt}_{n\to\infty} \chi_n(t) &= \lambda(t) = \int_0^1 (1-u)^k d(u\cos tu) = k \int_0^1 (1-u)^{k-1} u\cos tu \, du \\ &= k \frac{d}{dt} \int_0^1 (1-u)^{k-1} \sin tu \, du = k \Gamma(k) \frac{d}{dt} \left[ t^{-k} C_{k+1}(t) \right] . \dagger \end{split}$$

Again,  $nt^{-1}\mathbf{F}(t/n)\to\boldsymbol{\beta}$ , as  $n\to\infty$ , by the hypothesis (i); and it is a bounded function of (n,t). Thus, both factors of the integrand of the integral in the expression last given for  $\mathbf{I_2}$  being bounded, we may, when  $n\to\infty$ , integrate term by term, and get

$$\begin{split} & \underset{n\to\infty}{\text{Lt}} \, \mathbf{I_2} = \left[\beta t \lambda(t)\right]_0^{\mathbf{B}} - \beta \int_0^{\mathbf{B}} t \, \frac{d}{dt} \, \lambda(t) dt = \beta \int_0^{\mathbf{B}} \lambda(t) dt \\ & = \beta \, \Gamma(k+1) \left[ t^{-k} \mathbf{C}_{k+1}(t) \right]_0^{\mathbf{B}} = \beta \, \Gamma(k+1) \, \mathbf{B}^{-k} \mathbf{C}_{k+1}(\mathbf{B}), \end{split}$$

which is of the order  $B^{-k}$ , and is therefore as small as we please, B being chosen sufficiently large.

This proves the theorem.

§ 8. The companion theorem is as follows:--

THEOREM 2.—If b<sub>n</sub> is the typical coefficient of the Fourier sine series of an odd function, which is such that

(i) 
$$x^{-1} \int_0^x \left| d[xf(x)] \right|$$
 is a bounded function of x in the whole interval of periodicity, and

(ii) 
$$x^{-1} \int_0^x f(x) dx$$
 has a unique finite limit  $\beta$  as  $x \to 0$ ,

then  $(Ck)(nb_n) + 2\beta/\pi$ , when  $n \to \infty$ .

The proof is the same as that of the preceding article, sines taking the

\* In fact

$$\left| t \frac{d}{dt} \chi_n(t) \right| = \left| \sum_{r=1}^{n-1} \frac{r^2}{n^2} t \sin \frac{r}{n} t \left\{ (1 - r/n)^k - [1 - (r+1)/n]^k \right\} \right|$$

$$\leq \mathbf{B} \sum_{r=1}^{n-1} \left( [1 - r/n]^k - [1 - (r+1)/n]^k \right) \leq \mathbf{B}.$$

+ W. H. Young, "On Infinite Integrals involving a Generalisation of the Sine and Cosine Functions," Quart. Journ., vol. 43, p. 163 (1912).

See, for instance, my paper on "Successions of Integrals and Fourier Series," 'Proc. L.M.S., Ser. 2, vol. 11, p. 78, Cor. 1 (1912).

place of cosines. The only essential difference is in the expression for the function  $\lambda(t)$ . We now have

$$\lambda(t) = \int_0^1 (1-u)^k d(u \sin tu) = k \int_0^1 (1-u)^{k-1} u \sin tu \, dt$$

$$= -k \frac{d}{dt} \int_0^1 (1-u)^{k-1} \cos tu \, dt = -k \Gamma(k) \frac{d}{dt} [t^{-k} C_k(t)].$$

Whence

Lt 
$$I_2 = \beta \int_0^B \lambda(t) dt = \beta \Gamma(k+1) [1/\Gamma(k+1) - B^{-k}C_k(B)],$$

which, since B is as large as we please, so that the part of this expression involving B may be neglected, gives

$$Lt_{n\to\infty} I_2 = \beta.$$

This proves the theorem.

§ 9. THEOREM 3.—If an is the typical coefficient of the Fourier cosine series of an even function which is such that

(i) 
$$x^{-2} \int_0^x \left| d[xf(x)] \right|$$
 is a bounded function of x in the whole interval of periodicity, and

(ii) 
$$2x^{-2}\int_0^x f(v) dv$$
 has a unique limit  $\beta$  as  $x \to 0$ ,

then 
$$(C, 1+k)(n^2a_n) \rightarrow 2\beta/\pi$$
, as  $n \rightarrow \infty$ ,  $(0 < k < 1)$ .  
We have

$$\frac{\pi}{2}(C, 1+k)(n^2a_n) = \int_0^{\pi} \sum_{r=1}^{n-1} \left[ r^2 \cos rv - (r-1)^2 \cos (r-1) v \right] (1-r/n)^{1+k} f(v) dv$$

$$= \int_0^{\pi} \psi'_n(v) f(v) dv,$$

where

$$\psi_n(v) = \sum_{r=1}^{n-1} \left[ r \sin rv - (r-1) \sin (r-1) v \right] (1-r/n)^{1+k}.$$

By Theorem B1,  $n^k v^{1+k} \psi_n(v)$  is bounded for all positive values of v as  $n \to \infty$ .

Writing, as before,  $I_1$  and  $I_2$  for the two parts of the integral due to the intervals  $(B/n, \pi)$  and (0, B/n), we find, precisely as in the preceding article, that, as  $n \to \infty$ ,  $I_1$  approaches a limit or limits as small as we please, B being conveniently large.

The treatment of I<sub>2</sub> is the same as in the preceding article; we only have to notice that  $nt^{-2}\mathbf{F}(t/n)$  is now bounded, and that  $\chi_n(t)$  now stands for

 $n^{-2}\psi'_n(t/n)$ ,  $\psi_n(t)$  having the meaning attributed to it in the present article. The limiting function  $\lambda(t)$  is, therefore,

$$\lambda(t) = \lim_{n \to \infty} \chi_n(t) = \int_0^1 (1 - u)^{1+k} d(u^2 \cos t u) = -d^2 z / dt^2,$$

$$z = \Gamma(k+2) t^{-k-1} C_{k+1}(t).$$

Hence by the same process as in the preceding article,

Lt 
$$I_2 = \beta \int_0^B t \lambda(t) = \beta \left[ t \, dz / dt - z \right]_0^B$$
  

$$= \beta \Gamma(k+2) \left[ t^{-k-1} C_{k+1}(t) - t \, \frac{d}{dt} \, t^{-k-1} C_{k+1}(t) \right]_0^B$$

$$= \beta \Gamma(k+2) \left[ (k+2) \, t^{-k-1} C_{k+1}(t) - t^{-k} C_k(t) \right]_0^B.$$

Since B is as large as we please, the part due to the upper limit of integration may be neglected, and we get

Lt 
$$I_2 = \beta \Gamma(k+2)[(k+2)/\Gamma(k+2)-1/\Gamma(k+1)] = \beta$$
.

This proves the theorem.

§ 10. The companion theorem is the following:-

THEOREM 4.—If  $b_n$  is the typical coefficient of the Fourier series of an odd function which is such that

(i) 
$$x^{-2} \int_0^x \left| d[x f(x)] \right|$$
 is a bounded function of x in the whole interval of periodicity;

(ii) 
$$2x^{-2}\int_0^x f(x) dx$$
 has a unique limit  $\beta$  as  $x \to 0$ ;

then (C, 
$$1+k$$
)  $(n^2a_n) \rightarrow 0$ , as  $n \rightarrow \infty$ .

The proof is the same as that of the preceding article, cosines being replaced by sines.

The part  $I_1$  of the integral is, as before, negligible. In the calculation of  $I_2$ , the part due to the interval (0, B/n), the argument proceeds as before till we come to the calculation of the function  $\lambda(t)$ . We then have

$$\lambda(t) = \int_0^1 (1-u)^{1+k} d(u \sin tu)$$

$$= -\frac{d^2}{dt^2} (1+k) \Gamma(k+1) t^{-k-1} C_{k+2}(t),$$

whence, by the same reasoning as before, our present result follows, since  $t^{-k-1}C_{k+2}(t) = 0$ , when t = 0.

§ 11. The following theorem might be proved precisely in the same way as those which precede it. The proof here given is slightly different, and might equally well have been employed in the other cases.

**THEOREM** 5.—If  $a_n$  is the typical coefficient of the Fourier series of the even function f(x), which is such that

(i) 
$$x^{-3} \int_0^x \left| d \left[ x f(x) \right] \right|$$
 is bounded, and

(ii) 
$$3!x^{-3}\int_0^x f(x) dx$$
 has a unique limit  $\beta$  as  $x \to 0$ ;

then  $(C, 2+k)(n^3a_n) \rightarrow 0$ , as  $n \rightarrow \infty$ .

We have, as before.

$$\frac{\pi}{2}(C, 2+k) (n^3 a_n)$$

$$= \int_0^{\pi} \sum_{r=1}^{n-1} \left[ r^3 \cos r v - (r-1)^3 \cos (r-1) v \right] (1-r/n)^{k+2} f(v) dv$$

$$= \int_0^{\pi} \psi'_n(v) f(v),$$

where  $\psi_n(v) = \sum_{r=1}^{n-1} \left[ r^2 \sin rv - (r-1)^2 \sin (r-1) v \right] (1-r/n)^{k+2}$ 

Thus  $n^k v^{2+k} \psi_n(v)$  is bounded for all positive values of v. We divide the integral, as before, into two parts,  $I_1$  and  $I_2$ , where, integrating by parts,

$$I_{1} = \int_{B/n}^{\pi} \psi'(v) f(v) dv = \left[ n^{k} v^{2+k} \psi_{n} v \cdot v^{-2} f(x) \cdot n^{-k} v^{-k} \right]_{B/n}^{\pi} - \int_{B/n}^{\pi} \psi_{n}(v) df(v).$$

Here the quantity in square brackets may be neglected, for by (i)  $v^{-2}f(v)$  is bounded, and, by what has already been remarked,  $n^k v^{2+k} \psi_n(v)$  is bounded, so that the last factor,  $n^{-k} v^{-k}$ , determines the value, and this is as small as we please when n and B are taken sufficiently large. Also,

$$\int_{\epsilon}^{\pi} \psi_{\mathbf{n}}(v) \, df(v) = n^{-k} \int_{\epsilon}^{\pi} n^{k} \psi_{\mathbf{n}}(v) \cdot df(v) - 0, \text{ as } n \to \infty,$$

therefore, writing g(v) for the function of bounded variation vf(v).

$$I_{1} = \int_{B/n}^{e} \psi_{n}(v) df(v) = \int_{B/n}^{e} \psi_{n}(v) d[v^{-1}g(v)]$$

$$= \int_{B/n}^{e} \psi_{n}(v) v^{-1} dg(v) - q \int_{B/n}^{e} \psi_{n}(v) v^{-2}g(v) dv,$$

where the latter integral, being =  $\int_{B/n}^{c} n^k v^{2+k} \psi_n(v) \cdot v^{-2} f(x) \cdot n^{-k} v^{-1+k} dv$ , is

numerically less than a certain constant multiple of  $\int_{B/n}^{e} n^{-k} d(v^{-k})$ , which is again as small as we please.

On the other hand, writing  $G\left(v\right)$  for  $\int_{0}^{v}\left|\ dy\left(v\right)\ \right|$ ,

$$\left| \int_{\mathbf{B}/n}^{\epsilon} \psi_{n}(v) v^{-1} dg(v) \right| \leq \int_{\mathbf{B}/n}^{\epsilon} \left| n^{k} v^{k+2} \psi_{n}(v) \right| (nv)^{-k} v^{-2} dG(v) \leq K \left[ (nv)^{-k} \right]_{\mathbf{B}/n}^{\epsilon},$$

K being a constant. This is again as small we please. Thus, finally,  $I_1$  is numerically as small as we please, B and n being chosen sufficiently large. Again, changing the variable in calculating  $I_2$ , as before, and using  $\chi_n(t)$  for  $n^{-3}\psi'_n(t/n)$ , we see that  $t^3\frac{d}{dt}\chi_n(t)$  is bounded, and has for limiting function,

when  $n \to \infty$ ,  $t^3 \frac{d}{dt} \lambda(t)$ , where

$$\lambda(t) = \underset{n \to \infty}{\text{Lt}} \chi_n(t) = \int_0^1 (1-u)^{2+k} d(u^3 \cos tu) = (2+k) \int_0^1 (1-u)^{k+1} u^3 \cos tu \, du$$

$$= -\frac{d^8}{dt^3} (2+k) \int_0^1 (1-u)^{k+1} \sin tu \, du$$

$$= -\frac{d^3}{dt^3} \Gamma(3+k) t^{-k-2} C_{k+3}(t) = -\frac{d^3z}{dt^3}, \text{ say.}$$

We thus get

$$I_{2} = \int_{0}^{B/n} \psi'_{n}(v) f(v) dv = \int_{0}^{B} \chi_{n}(t) n dF(t/n)$$

$$= \left[ \chi_{n}(t) n F(t/n) \right]_{0}^{B} - \int_{0}^{B} n t^{-8} F(t/n) \cdot t^{3} \frac{d}{dt} \chi_{n}(t) dt.$$

Proceeding to the limit, and integrating on the right term by term, we get

$$3 \operatorname{Lt}_{n \to \infty} \mathbf{I}_{2} = \left[ \lambda(t) t^{3} \beta \right]_{0}^{\mathbf{B}} - \int_{0}^{\mathbf{B}} \beta t^{3} \frac{d}{dt} \lambda(t) dt$$
$$= \left[ \lambda(t) t^{3} \beta \right]_{0}^{\mathbf{B}} - \int_{0}^{\mathbf{B}} \frac{d}{dt} \left[ t^{3} \lambda(t) - 3t^{2} \lambda(t) \right] dt,$$

whence

Lt 
$$I_2 = \frac{1}{2}\beta \int_0^B t^2 \lambda(t) dt = -\frac{1}{2}\beta \int_0^B \frac{d}{dt} \left( t^2 \frac{d^2z}{dt^2} - 2t \frac{dz}{dt} + 2z \right) dt$$
.

The value of  $t^2z''-2tz'+2z$  at the upper limit of integration is as small as we please, provided B be sufficiently large. We are therefore only concerned with its value at the origin, which is easily seen to be zero. This proves the theorem.

§ 12. The companion theorem is the following:—

**THEOREM 6.**—If  $b_n$  is the typical coefficient of the Fourier series of the odd function f(x), which is such that

(i) 
$$x^{-3} \int_0^x \left| d[xf(x)] \right|$$
 is bounded, and

(ii) 
$$3!x^{-3}\int_0^x f(x) dx$$
 has a unique limit  $\beta$  as  $x \to 0$ ,

then 
$$(C, 2+k)(n^3b_n) \rightarrow 2\beta/\pi$$
, as  $n \rightarrow \infty$ .

As in the corresponding earlier theorems, we now only have to change the cosines into sines. There is no alteration of interest till we come to the expression for the function  $\lambda(t)$ . We then have

$$\begin{split} \lambda\left(t\right) &= \int_0^1 (1-u)^{2+k} d\left(u^3 \sin t u\right) = (2+k) \int_0^1 (1-u)^{1+k} u^3 \sin t u \, du \\ &= + \frac{d^3}{dt^2} (2+k) \int_0^1 (1-u)^{k+1} \cos t u \, du = \frac{d^3}{dt^3} \Gamma(3+k) t^{-k-2} \, C_{k+2}(t) = \frac{d^3 z}{dt^3}, \, \text{say}. \end{split}$$

We thus get

$$\begin{split} & \underset{n \to \infty}{\text{Lt }} \mathbf{I}_2 = \tfrac{1}{2}\beta \int_0^{\mathbf{B}} t^3 \lambda\left(t\right) dt = \tfrac{1}{2}\beta \left[ t^2 z'' - 2tz' + 2z \right]_0^{\mathbf{B}} \\ & = \tfrac{1}{2}\beta \Gamma\left(3+k\right) \left[ (k+4)(k+3) t^{-k-2} \mathbf{C}_{k+2}(t) - 2(k+3) t^{-k-1} \mathbf{C}_{k+1}(t) + t^{-k} \mathbf{C}_k(t) \right]^{\mathbf{B}}. \end{split}$$

As before we need only retain the part of this expression due to the origin, which is

$$\frac{1}{2}\beta[(k+4)(k+3)-2(k+3)\Gamma(k+3)/\Gamma(k+2)+\Gamma(k+3)/\Gamma(k+1)] = \beta.$$

This proves the theorem.

§ 13. The general theorem and its companion theorem are now evident. We may add that these theorems may be deduced from one another by an inductive process. I have purposely adopted the procedure in the text, as the processes employed seem to be sufficiently instructive in themselves to be worthy of publication.

# The High-Frequency Resistance of Multiply-Stranded Insulated Wire.

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#### INTRODUCTORY.

Conductors which have to carry high-frequency currents are often made up of a large number of separately insulated fine wires stranded together, with the object of compelling the current to distribute itself over the whole cross-section of the conductor. This may be done for two different reasons: firstly, to decrease the variation of inductance and resistance with change of frequency; and, secondly, to decrease the effective resistance of the conductor at high frequencies. To be effective, it is necessary that every wire should occupy in turn the same relative position in the conductor, so that the electromotive force induced in each wire by the magnetic flux should have the same average value over the whole length of the wire. If every separate wire has the same resistance, the same applied P.D. and the same induced E.M.F., both in amplitude and phase, they will all necessarily carry the same current, and the total current will therefore be uniformly distributed between all the wires.

The usual method of obtaining this similarity in the path of every strand is to make a conductor of three, four, or five wires twisted together, and then to twist three such conductors together, and so on until the resulting conductor contains the required number of wires. A large number of such multiple conductors are sometimes plaited or braided into a tubular conductor. Two of the individual wires of such a conductor may be in contact, except for the insulation, at a certain point, and then again further on at another point, one wire having followed an internal and the other an external path between the two points. From a knowledge of the current, frequency, and projected area of the loop formed by the two wires, measured normal to the magnetic flux, the E.M.F. induced in the loop can be calculated; thus, if the multiple conductor has a diameter of 1 cm. and is wound into a coil with one turn per centimetre, and if the current is 100 amperes at a frequency of 106, the E.M.F. induced in a loop of 5 sq. cm. is about 20 volts, giving 10 volts between the wires at each point of contact. In circuits containing spark-gaps the rate of change of the current may reach very high values and thus cause much greater potential differences between

the separate strands, which must therefore be efficiently insulated to prevent sparking between them.

A single copper wire 0.01 cm. diameter has a resistance, at a frequency of 500,000, differing very little from its resistance to continuous current. It must not be assumed, however, that the same is true of a conductor made up of a number of these fine insulated wires, however perfectly they may be stranded or plaited together. That the effective resistance of such conductors at high frequencies may be considerably greater than with continuous currents has been known for some time, but little was known which would enable a designer of high-frequency apparatus to decide between a solid wire and different types of multiply-stranded wire. In this paper simple formulæ are established and Tables given by means of which the effective resistance of such conductors can be determined, and the size and number of strands chosen so as to give the best results under the specified conditions.

When a high-frequency current is passed through a single solid wire, the current is confined more and more to the outer part as the frequency is raised, leaving the inside free from both current and magnetic flux. the wire is situated in the immediate neighbourhood of a number of other wires carrying high-frequency current it will be exposed to the magnetic field due to the latter, which will induce eddy-currents in it. Assuming the wires to be approximately parallel, these eddy-currents will pass up one side of the wire and down the other, adding to the energy dissipated in the wire, without affecting the total current passing through it. That the loss due to the eddy-currents is simply added to that due to the main current can be shown as follows. Let  $\sigma_1$  be the uniform density of the main current, and  $\sigma_2$ the density at any point of the superimposed eddy-current; the integral of the former over the cross-section of the wire is the main current, whilst that The loss of power per centimetre of the wire is of the latter is zero.  $((\sigma_1 + \sigma_2)^2 \rho dS)$ , where dS is an element of cross-section; this is equal to  $[\sigma_1^2 \rho dS + [\sigma_2^2 \rho dS]$ , since  $2\sigma_1[\sigma_2 dS]$  is zero. With alternating current this is true at every instant, so that the losses, as calculated from the root-meansquare values of the currents, may be added without any question as to the phase of the various currents.

The magnetomotive force due to the eddy-currents will tend to oppose the passage of the flux and to force it to pass on either side of the wire without going through it. For this reason, calculations based on the assumption that the distribution of the magnetic flux is unaltered by the eddy-currents are

<sup>\*</sup> Meissner, 'Jahrbuch der Drahtlosen Telegraphie,' 1909, p. 57; Lindemann, 'Deut. Phys. Gesell.,' 1909, p. 682; 1910, p. 572; 'Jahrbuch der D. T.,' 1911, p. 561; Moller, 'Ann. der Physik,' vol. 36, p. 738 (1911); 'Jahrbuch der D. T.,' 1914, p. 32.

only applicable up to a certain point, beyond which the actual flux distribution must be taken into account. In the first part of this paper it is assumed that the flux distribution is unaltered by the eddy-currents which it produces, and the effective resistance of a multiply-stranded conductor both when straight and when coiled is calculated on this assumption. Formulæ are then established for the best space-factor to adopt when making such conductors and for the minimum resistance thereby obtained. The results are then tabulated for general use. In the second part of the paper, the problem is solved in a more general manner, taking into account the effect of the eddy-currents in modifying the magnetic field within the conductor; it is shown, however, that this precaution is unnecessary for the majority of the cases tabulated in Part I.

#### List of Symbols Employed.

All symbols referring to alternating magnitudes represent their maximum values unless otherwise stated.

```
\alpha = space factor of conductor = \frac{\text{cross-section of copper}}{\text{total cross-section}}
```

B = density of magnetic flux.

d = 2r = diameter of each single strand, bare (cm.).

 $d_1 = \text{diameter of each single strand, insulated (cm.)}.$ 

D = diameter of multiple conductor (cm.).

f = frequency, cycles per second.

H = magnetic force at any point.

I = main current carried by multiple conductor (amperes).

 $j=\sqrt{(-1)}.$ 

 $\mu = \text{permeability}.$ 

n = number of separate wires in multiple conductor.

 $\omega = 2\pi f$ .

 $\Phi = \text{magnetic flux}.$ 

 $\rho$  = specific resistance in ohms per centimetre cube.

 $R_o$  = resistance of multiple conductor to continuous current.

 $R_f$  = resistance of straight multiple conductor to alternating current.

 $R_c$  = resistance of coiled multiple conductor to alternating current.

R<sub>so</sub> = resistance of solid conductor of same overall diameter to continuous current.

R<sub>v'</sub> = resistance of solid conductor of same overall diameter to alternating current; conductor straight.

 $R_{*\sigma} = {
m resistance} \ {
m of} \ {
m solid} \ {
m conductor} \ {
m of} \ {
m same} \ {
m overall} \ {
m diameter} \ {
m to} \ {
m alternating}$ 

S = turns per centimetre in coils.

 $\sigma$  = current density in amperes per square centimetre.

t =side of square individual strand (cm.).

 $\tau = \text{side of square multiple conductor (cm.)}$ .

#### PART I.

Consider a length of 1 cm. of a long solid wire of diameter d situated in

an alternating magnetic field of strength H at right angles to the length of the wire. The E.M.F. induced in the rectangle d cm. wide and 1 cm. long (see fig. 1) is  $\Delta E = \omega H d \ 10^{-8}$  volts, and the current density at the outer edges of the wire due to this induced E.M.F. is  $\sigma = \Delta E/2\rho$  amperes per cm.<sup>2</sup>. At any point in the wire at a distance y from the plane through its axis, parallel to H,

$$\sigma = \frac{\Delta E}{2\rho} \cdot \frac{y}{r} = \frac{\omega H y}{\rho}$$
. 10<sup>-8</sup> amperes per cm.<sup>2</sup>.

The loss per cubic centimetre due to this current is

$$\frac{\sigma^2 \rho}{2} = \frac{\omega^2 H^2 10^{-16}}{2\rho}$$
.  $y^2$  watts,

that in the strip of width dy, breadth  $2r\sin\phi$ , and length 1 cm. (see fig. 1) is

$$\frac{\omega^2 \mathrm{H}^2 10^{-16}}{2\rho} \cdot y^2 \cdot 2r \sin \phi \, dy \text{ watts,}$$

and that in the whole wire per centimetre of length

$$\frac{H^2 \omega^2 \pi r^4 10^{-16}}{8\rho} \text{ watts.} \tag{1}$$

Straight Stranded Conductor of Circular Section.

At any point within a straight conductor of circular section, at a distance x from the axis, the magnetic force due to its own current is  $H = Ix/5R^2$ . It is assumed that the individual strands are approximately parallel to the axis of the cable, in which case H is perpendicular to the axis of each strand as assumed in fig. 1. The average value of  $H^2$  taken over the whole cross-section of the cable is

$$\frac{1}{\pi R^2} \int_0^R \dot{H}^2 \cdot 2\pi x \cdot dx = \frac{I^2}{50R^2}.$$
 (2)

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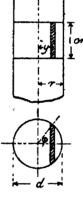


Fig 1

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Substituting this in equation (1), we find for the average loss in a ventimetre length of single wire,

$$\frac{I^3\omega^2\pi r^4}{400\rho R^2}$$
. 10<sup>-16</sup> watts.

This is due only to the self-induced eddy-currents; the loss due to the main current I/n in 1 cm. of single wire is

$$\frac{\mathbf{I}^2}{2n^2} \cdot \frac{\rho}{\pi r^2}$$
 watts.

Hence the total loss in 1 cm. of single wire is

$$\frac{\mathrm{I}^2}{2n^2} \left( \frac{\rho}{\pi r^2} + \frac{\omega^2 \pi r^4 n^2 10^{-16}}{200 \rho \mathrm{R}^2} \right).$$

In 1 cm. of the whole cable the loss is n times as great.

Hence 
$$R_f = R_o \left( 1 + \frac{\omega^2 \pi^2 r^6 n^2 10^{-16}}{200 \rho^2 R^2} \right),$$
 (3)

which, for copper ( $\rho = 1.7 \cdot 10^{-6}$ ) may be written

$$R_f = R_o (1 + 4 \cdot 2 \cdot 10^{-6} \cdot n^3 f^2 d^6 / D^3),$$
  
=  $R_o (1 + 4 \cdot 2 \cdot 10^{-6} \cdot n f^2 d^4 \alpha),$  (3a)

where  $\alpha = nd^2/D^2$  is the space factor.

Closely-Wound Long Single-Layer Coil.

It is assumed for simplicity that the conductor has a square cross-section, and that adjacent turns are in actual contact, as shown in fig. 2. Let x be

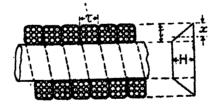


Fig 2

the distance from the outer surface of any point within the conductor, then at this point

 $\mathbf{H} = \frac{4\pi \mathrm{IS}}{10} \cdot \frac{x}{\tau}$ 

and the average value of H<sup>2</sup> over the whole cross-section of the square conductor is

$$\frac{16\pi^2 I^3 S^2}{100} \cdot \frac{1}{3},\tag{4}$$

which, substituted in equation (1), gives for the average loss in a centimetre length of single wire

 $\frac{\pi^{3}I^{2}S^{2}\omega^{2}r^{4}10^{-16}}{150\rho}$  watts.

For 1 cm. of the whole conductor it will be n times as great. This is the loss due to the self-induced eddy-currents only, the total loss in 1 cm. length of the stranded conductor is

$$\frac{I^{2}}{2} \cdot \frac{\rho}{n\pi r^{2}} + \frac{I^{2}S^{2}\omega^{2}r^{4}n\pi^{3}10^{-16}}{150\rho} \text{ watts.}$$

$$R_{c} = R_{o} \left( 1 + \frac{4\pi^{4}r^{6}\omega^{2}S^{2}n^{2}10^{-18}}{3\rho^{2}} \right). \tag{5}$$

Hence

For copper, this may be written

$$R_{o} = R_{o} (1 + 28 \cdot 10^{-6} n^{2} f^{2} S^{2} d^{6})$$

$$= R_{o} (1 + 35 \cdot 6 \cdot 10^{-6} n f^{2} d^{6} \alpha), \tag{5a}$$

since  $\alpha \tau^2 = n\pi d^2/4$  and, if the adjacent turns are in contact,  $S\tau = 1$ .

If not closely wound, i.e., if  $S\tau < 1$ ,  $S^2d^2 = (S\tau)^2/n$ .  $d^2/d_1^2$ , since, assuming the small wires to be arranged as shown in fig. 2,  $\tau^2 = nd_1^2$ . If the space between adjacent turns is small, the formula for H will still be approximately correct, and

$$R_c = R_o [1 + 35.6 \cdot 10^{-6} \cdot n f^2 d^4 \alpha (S\tau)^2]. \tag{5b}$$

As an example of the use of this formula, it can be applied to an experimental result obtained by Lindsmann (loc. cit.). He found that 14 turns of stranded conductor wound on a glass cylinder 24 cm. diameter, had a resistance at a frequency of 900,000 cycles per second, 15 times its continuous current value. The conductor consisted of 180 enamelled wires 0.012 cm. diameter, arranged  $3 \times 3 \times 4 \times 5$ , i.e., five single wires were twisted together, then four of these conductors, and so on. For a single wire 0.012 cm. diameter at a frequency of 900,000,  $d\sqrt{f} = 11.4$ , from which it can be shown that if wound singly into a solenoid, the increase in resistance due to skin effect would be about 10 per cent. Applying the formula just found for a stranded wire solenoid, viz.:

$$R_o = R_o \{1 + 35.6 \cdot 10^{-6} \cdot n f^2 d^4 \alpha (S\tau)^2 \},$$

assuming  $\alpha = 0.5$  and  $S\tau = 0.9$ , since, although the turns are in contact, the conductor is round and not square, we have

$$R_o = R_o (1 + 43.1).$$

Now the above expression applies only to a very long solenoid, whereas the coil tested by Lindemann was a narrow one of large diameter, for which it can be readily shown that the magnetic field strength at the inner side of

the wire is little more than half that in a long selenoid. The eddy-current losses would therefore be a little more than a quarter of those calculated for a long selenoid. This agrees approximately with the value  $R_c=15~R_o$  found experimentally.

Now a solid wire with the same cross-section of copper has a diameter of 0.16 cm. At the same frequency  $d\sqrt{f}$  would be 153, and  $R_e/R_o$  for a long solenoid would be about 13 or 14. Hence, in this case, the stranded conductor is much inferior to the solid wire with the same cross-section of copper; in the same space, however, a solid wire of greater cross-section could be wound, thus further reducing the resistance, whilst the cost would be but a fraction of that of the stranded wire.

It will be seen from equations (3a) and (5a) that, for given values of d and  $\alpha$ , the ratio  $(R_f-R_o)/R_o$  of the increase in resistance to the continuous current resistance is proportional to n, the number of wires in the conductor; hence the difficulty increases with the current for which the conductor is to be designed. If the total cross-section, including insulation and air space, remains unchanged, and the space factor is maintained constant, n will vary inversely as  $d^2$ , and the percentage increase of resistance will be proportional to  $d^2$  or inversely proportional to n. The diameter of the individual strands, however, can hardly be reduced below about 0.005 cm., on account of manufacturing difficulties.

If the overall diameter of the cable and the diameter of the wire to be employed are fixed, it is important to note that it is not necessarily beneficial to crowd as many wires as possible into the available space. The best value of n or of the space factor  $\alpha$  can be calculated in each case as follows. It has been shown that

$$\mathbf{R}_f = \mathbf{R}_o (1 + kn f^2 d^4 \alpha),$$

where k=4.2,  $10^{-6}$  for a straight conductor of copper and 35.6,  $10^{-6}$  for a very closely wound long solenoid with a conductor of square section. Now, if the resistance to continuous current of a solid wire of the same overall diameter is  $R_{so}$ ,

$$\alpha = \frac{R_{so}}{R_o}, \quad \frac{n}{\alpha} = D^2/d^3,$$

$$R_f/R_{so} = \frac{1}{\alpha} + knf^2d^4,$$

$$= \frac{D^2}{nd^3} + knf^2d^4.$$
(6)

and

For this to be a minimum with given values of D and d, it is necessary that

$$n = \frac{1}{\sqrt{k}} \cdot \frac{D}{fd^3}.$$
 (7)

If n is made greater than this, the resistance to high-frequency currents will not be decreased but increased. As an example, a conductor 0.5 inch diameter, made up of wires 0.01 cm. diameter, for a frequency of 500,000, should have n = 1240, which corresponds to a space factor of only 0.077.

The best value of the space-factor in any given case is given by the equation,

$$\alpha = \frac{nd^2}{D^2} = \frac{1}{\sqrt{k}} \cdot \frac{1}{fdD}.$$
 (8)

If the space-factor has this optimum value, then

$$R_f/R_o = 1 + kn\alpha f^2 d^4 = 1 + 1 = 2,$$
 (9)

and 
$$R_f/R_{so} = R_f/R_o \times R_o/R_{so} = \frac{2}{\alpha} = 2\sqrt{k} \cdot f dD.$$
 (10)

On substituting in equations (8) and (10) the values found above for k, it is seen that, for a straight conductor of copper, the optimum space factor is

$$\frac{487}{fdD},\tag{11}$$

and

$$R_f/R_{so} = \frac{2fdD}{487},\tag{12}$$

whilst for a single-layer solenoid wound with a conductor of square section, with  $S\tau = 0.71$ , k = 17.8.  $10^{-6}$ , the optimum space-factor

$$=\frac{238}{fdD'}\tag{13}$$

and

$$R_c/R_{so} = \frac{2fdD}{238}.$$
 (14)

[Note.—If it is assumed that round conductor is equivalent to square of the same cross-section, then  $S\tau = 0.88 \text{ SD}$ , and equations (13) and (14) are applicable to round conductors with SD = 0.8].

These values of  $R_f/R_{so}$  are only true if the conductor is made with the optimum space factor, and this depends on the frequency, and on whether the wire is straight or coiled, and, in the latter case, on the details of the winding. The values of the ratios

$$A = \frac{A.C. \text{ resistance of stranded cable}}{C.C. \text{ resistance of stranded cable}} = \frac{R_f}{R_o} \text{ or } \frac{R_o}{R_o}$$

$$B = \frac{A.C. \ resistance \ of \ stranded \ cable}{C.C. \ resistance \ of \ solid \ conductor} = \frac{R_f}{R_{so}} \quad or \quad \frac{R_c}{R_{so}}$$

$$C = \frac{A.C. \ resistance \ of \ solid \ conductor}{C.C. \ resistance \ of \ solid \ conductor} = \frac{R_{sf}}{R_{so}} \quad or \quad \frac{R_{sc}}{R_{so}}$$

have been calculated for a number of typical cases, and the results are given

in the Tables. The solid conductor is assumed to have the same overall diameter as the stranded cable, and therefore capable of replacing it in any coil or apparatus. Four values of the overall diameter D have been taken, viz., 0.1, 0.2, 0.5, and 1 cm., and three alternative sizes of wire, viz., 0.005, 0.01, and 0.02 cm. The wave-lengths chosen are 300, 600, 1200, 3000, and 6000 metres. Below the heavy stepped line the space factors have been assumed to have the calculated optimum value; above the stepped line this calculated value was considered impossibly high, and the resistance has therefore been calculated for three alternative values of a, viz., 0.1, 0.25, and In such cases it is best to make a as large as possible. The coils are assumed to be long solenoids, with a single layer of square conductor, having a ratio of side to pitch of 0.71, which is approximately equivalent to round conductor, with a diameter equal to 0.8 of the pitch. With a more open winding or with shorter coils, the results would lie between these and those obtained for the same conductor when straight.

A comparison of the columns headed B and C in the Tables shows in each case the advantage, if any, to be gained by using insulated stranded conductor. The ratio of B to C is the ratio of the high-frequency resistance of the strand to that of the solid wire, which could be used in its place. If d = 0.02 cm., B is larger than C for wave-lengths below 1200 metres, but smaller than C for longer wave-lengths, that is to say that, even if made with the ideal space factor, the stranded conductor is inferior to the solid wire at the shorter wave-lengths. If d = 0.01 cm., the stranded conductor, if correctly made for the given conditions, is on a par with the solid conductor at short wave-lengths, and may be considerably better at longer wave-lengths. With the finest wire, viz., d = 0.005 cm., the stranded conductor may have a resistance much lower than that of the solid wire.

It will be noticed that for a solenoid wound with stranded conductor of 1.0 cm. diameter, made up of wires of 0.02 cm. diameter, the lowest resistance at a wave-length of 300 metres is obtained by making the space-factor 0.012, and that, even if made with this optimum space-factor, the high-frequency resistance is 168 times as great as the continuous-current resistance of a solid conductor of the same size, whereas the high-frequency resistance of the latter would be only 100 times its continuous-current value. The solid conductor could be replaced by a thin tube, since the depth of penetration into copper at a frequency of 106 is only about 0.03 cm. Hence it appears that it is only by using wires as small as 0.005 cm., and by stranding them together with a certain space-factor, that conductors for a frequency of a million can be made to have a lower effective resistance than solid wires or tubes occupying the same space.

Table 1 Straight Conductor. d = 0.005 cm.

Ä	!	$f = 10^6$ $\lambda = 300$	9.96 E			f = 5 $\lambda = 60$	5 × 10 <sup>6</sup> . 600 m.			ζ = 2. λ = 128	2 ·5 × 10 <sup>5</sup> . 1200 m.			λ = 30 λ = 30	10°. 3000 ш.	AND ASSESSED TO SERVICE AND ASSESSED.		$f = 5 \times 10^4$ , $\lambda = 6000  \text{m}$ .	× 104.	
	ď	4	gi	ರ	d	4	mi	ပ်	a	Ą	æ.	ပ်	ď	Ä	æ	ပ်	ei ei	4	œ.	<b>:</b>
cup. 0 · 1	0.1 0.25 0.5	1.01 1.06 1.38	1.01 1.04 2.03	4 4 4 66 86 86	0.35	95 5	10 0 4 06 2 13	81 81 81 14 12 12	00.12		04%	2 · 15 2 · 15	0.1 0.2 0.5		51 4 ss	353	0.1 0.25 0.5	pd mt mt	544	1.16 1.16 1.16
çı O	<b>9</b> .0	69	<u>:</u>	7 -85	0 ·1 0 ·25 0 ·5	1 01 1 06 1 26	10 ·1 4 ·26 2 ·52	5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5	0.1 0.25 0.5	1.01	10 4 · 06 2 · 13	4 4 30 30 30 30	0.1 0.25 0.6		54%	2 2 2 3 2 3 5 3 5 5 3 5 5 3 5 5	0 0 0 5 5 5		Ö 4 81	1 96 1 96 1
ò	**	o)	10 ·2	19.2	<b>\$.</b> 0	01	1. 9	13 6	0.1 0.25 0.5	1.02	01 4 8 4 4 8	9.75 9.75	0.1 0.25 0.5	1.05	10	6.25 6.25 6.25	0 ·1 0 ·25 0 ·6		01 4 84	444 ល់សំល់
1.0	0.1	N	20.55 50	₹N 98	\$ 0	Ŋ	10 :2	7.	<b>7.</b> 0	0)	5.1	19 ·2	0 0 ii	1 1.06 1.25	10 2 4 25 2 5 5	2223	0.5	1.02	10 4.1	8 75 8 75 8 75

		$f = 10^6.$ $\lambda = 300  \text{m}$	10°. 300 m.		PITOR HOTOLOGIA NA S	λ = 5 = 6	$f = 5 \times 10^4.$ $\lambda = 600 \text{ m}.$	ought the set of		$f = 2.1$ $\lambda = 129$	$f = 2.5 \times 10^{5}$ . $\lambda = 1200 \mathrm{m}$ .	. "		$\int_{\lambda} = 16$	10°. 3000 m.		•	f = 5 λ = 6	5 × 10 <sup>4</sup> . 6000 m.		
į.	ď	4	B.	C.	ď	Α.	æi.	ن	ď	4	pi,	_ ່ ວ	ď	Α.	æi	ڼ	ď	¥.	. 18	Ċ	
9	9	84	÷	<b>4</b>	0.1 0.25 0.5	1.06	10·1 4·26 2·52	2 94 2 94 2 94	0.1 0.25 0.5	1.01	10 4·06 2·13	2 15 2 15 15	0.1 0.25 0.5		01 4 83	1.45	0.1 0.25 0.5		0144	1.16 1.16 1.16	
0	. O	64	φ 9)	7 85	<b>65</b> .0	87	4.1	2 . 62	0.1 0.25 0.5	1 2 3 8 8	10·1 4·26 2·52	4 4 05 80 4 4	0.1 0.25 0.6	1:05	10 4.8	2.65 2.65 2.65	0.1 0.25 0.5	<b></b>	04 4 91	1 95 1 95 1 95	
0		N	<b>9</b> 80	7.61	<b>7.</b> 0	89	10.2	13.6	<b>†</b> . 0	N N	5.12	9.75	0·1 0·25 0·5	1.26	10 4 · 26 2 · 52	6 25 6 25 6 25	0·1 0·25 0·5	1 02 1 05	10 4·1 2·1	444 io io io	
•	96.0	<b>09</b>	4	38 -2	0.1	6)	90.9	27.1	6.5	<b>\$4</b>	10.2	9. 8.	67.0	83	. <del>4</del>	12.2	0 ·1 0 ·25 0 ·5	1 1.06 1.26	10 4 26 2 52	8.73 8.75 8.75	

Table III. Straight Conductor. d = 0.02 cm.

	$f = 10^6.$ $\lambda = 300.$	10°. 300 m.			) = 6 \ \ = 6	$f = 5 \times 10^{6}$ . $\lambda = 600 \text{ m}$ .		-	$f = 2.5 \times 10^{\circ}$ . $\lambda = 1200 \text{ m}$ .	5 × 10°. 30 m.			$f = 10$ $\lambda = 30$	10°. 3000 m.			$f = 5 \times 10^4$ . $\lambda = 6000 \text{ m}$ .	× 104. 300 m.	
	Ą	рĠ	ပံ	<b>ਬੰ</b>	4	щ	<b>છ</b>	8	¥	æi	ບ່	ď	4	<b>m</b> i	ပ	ď	×.	æi	Ö,
cm. 0.1 0.24	59	7. 80	4.05	÷.	64	-	2 94	2.94 0.1 0.25 0.5	1.00	10·1 4·26 2·52	2 2 5 2 15 5 15 5 15	2·15 0·1 2·15 0·25 2·15 0·5	1 1 6	10	333	0.1 0.25 0.5	hand band hand	01 4 2	1.16
0.12	N	<b>7</b> . 91	7.86	48.0	69	80 53	5 62	97.0	8	<b>-</b>	4.05	0.1 0.25 0.5	1.01 1.05 1.15	10 .1 2 .2 3 :3	2 65 2 65 65	0 · 1 0 · 25 0 · 5	1 05	10 4 2·1	1.95 1.95 1.95
0 -05	N .	4	19.2	0.1	N	30.2	13 ·6	2.	N	70.5	9.75	4.0	67	4.1	6 .25	0.1 0.25 0.5	1.06	10 4 · 26 2 · 52	444 iò iò iò
1.0 0.025	83	28	38 :2	90.0	83	4	27 -1	0.1	64	20.5 19.2	2.61	0.24	63	œ 63	12.2	0.48	87	4.1	4.1 8.76

Table IV. Single Layer Long Solenoid. d = 0.005 cm.

۴	•	$f = 10^6.$ $\lambda = 300.$	96. 100. 11.		ng pang silikat a manghilikanakan sa	$f = 5 \times 10^5$ . $\lambda = 600 \text{ m}$ .	× 10 <sup>5</sup> .			$f = 2.5 \times 10^{\circ}$ . $\lambda = 1200  \text{m}$ .	6 × 10°. 00 m.			λ π π 3	10 <sup>6</sup> . 3000 m.	ed-thra∷athab		7. = 5. = 60	5 × 10°. 6000 m.	
<b>-</b>	븅	4	æi		ď	A.	B.	ပ်	હં	¥	æi	ر.	ਚੰ	¥	pci	ပ်	é	4	pei .	ပ
9.0	64.0	89	4.	9.6	0.1 0.25 0.5	1 01 1 07 1 27	10·1 4·3 2·5	က ဆေး က ဆဲ ဆား ဆုံ	0·1 0·25 0·5	- 1 1 63	02 4.11 1.12	444	0 0 1,5 0 0 0 0		0 <b>4</b> 8	<b>99</b> 89 89			548	જા જા જા જાં જાં જાં
Ġ Ġi	77.0	Ø	<b>3</b>	8	6 <del>‡</del> .0	N	2.5	14	0 ·1 0 ·25 0 ·5	1.01	10.1 \$-8 2.5	9.6 9.6 9.9	0.1 0.25 0.5	1 .05	10 2 · 1	စ္စ	0.25		348	न् च्चे धंधंधंधं
6	0.1	ο <b>ι</b>	22	<b>9</b>	0.5	64	10.5	ž.	4.0	613	5.2	25	0.1 0.25 0.5	1.01	10·1 4·3 2·5	16 16 16	0.1 0.3 0.5	1 1 68	10 4 · 1 2 · 1	===
9	<u>ර</u> දි	61	3	100	0.1	64	22	۲	£ 0	8	10.5	8	0.48	M	4.2	32	0.1 0.25 0.5	1.01	10 · 1 4 · 3 2 · 5	<b>a</b> aa

Table V. Single Layer Long Solenoid. d = 0.01 cm.

c		f = 10°. λ = 300 m.	90 H			ر ا = 5 ا = 6	$f = 5 \times 10^{3}$ . $\lambda = 600  \text{m}$ .			$\int_{\lambda} = 2$	2.5×10 <sup>4</sup> . 1200 m.	and the second		) 	$f = 10^{6}$ . $\lambda = 3000  \text{m}$ .		., ,	/ = 5 λ = 6	$f = 5 \times 10^6$ . $\lambda = 6000  \text{m}$ .	
	d	Ą.	<b>m</b>	Ö	E .	₹	æ	ပ	ď	Ą	æi	ပ်	aj	4	pi mi	ပ်	d	4	æ	ರ
<b>1</b> .0	72.0	64	œ 4	9.6	67.0	a	44 63	8. 80	0 · 8 5 0 · 5	1.01	10.1 10.4 20.3	444	0·1 0·25 0·5	1 1 2	01 4.2	හා හා හා	000	perior paral	54.8	00 00 00 00 00 00
0.2 2.0	0.13	et	16.8	8	77.0	<b>81</b>	∞ 	2	0.40	Ħ	4.2	9.6	0.25	1.01	01 1: 04 82 1: 04 85	တက္ တ	0.25 0.55	1 1 0	10 4 2 · 1	444 ùùù
9.0	90.0	83	3	<b>26</b>	0.1	es .	8	88 88	67 O	83	10.5	ĸ	67-0	87	<b>4</b> 2.	16	0.25 0.6	1 01	10.1 4.3 5.5	===
Ģ	1.0 0.032	89	25	100	0.0	N	42	7	0.1	81	21	26	0.25	84	4.8	328	0.49	2	4.2	22

Table VI. Single Layer Long Solenoid. d=0.02 cm.

F		$f = 10^6.$ $\lambda = 300  \text{m}.$	10°. 300 m.	-	a reductive recorded	$f = 5 \times 10^{9}.$ $\lambda = 600  \text{m}.$	× 10°. 10°. 11°.		Contain 6	$ \int = 2 $ $ \lambda = 15 $	$f = 2.5 \times 10^{\circ}$ . $\lambda = 1200  \text{m}$ .			1 H	3000 m.			$J = 0 \times 10^{\circ}.$ $\lambda = 6000 \text{ m}.$	200 E.	
3	ď	¥	pá	ຍ	ei ei	₹.	æ	G.	ď	4	ei —	ن	ti	Ψ.	pi pi	ວ່ ້	ä	Α.	B.	Ċ
g T	cm. 0·12	84	16.8	9.6.	<b>7</b> 6.0 9.6	63	∞ 4.	% .0	67-0	24	. <del>4</del>	7.4	0.25	1.01 1.05 1.18	01 1. 2. 2. 2.	m m m	0.1 0.25 0.5	1 1 05	10 4 2·1	લ્લ લ્લ લ્લ લ્લ લ્લે લ્લે
Φ έ2	90-0	<b>c</b> 9	88 æ	ន្ត	0.18	69	16.8	<b></b>	<b>7</b> 7.0	69	**	9.6	<b>6</b> <del>7</del> .0	87	7. 8	9	0.25 0.35	1.01 1.05 1.18	10·1 4·2 2·3	4 4 4 3 5 5 5
19	0.5 0.025	. 03	<b>3</b> 5	8	0.02	প	<b>4</b>	ĸ	1.0	81		23	17.0	N	**	16	0.49	04	4.2	11
Ó	1.0 0.012	63	891	92	0.025	63	ま	7	0.02	<b>89</b>	77	<b>3</b> 2	0.12	N	16.8	32	<b>4</b> %. 0	e4	<b>7.</b> 8	22

The following Tables illustrate the effect of varying-

- (a) The space-factor a, by varying n, whilst keeping D and d constant;
- (b) The number of wires n, and therefore also D, whilst keeping d and  $\alpha$  constant; and
  - (c) The frequency f only.

Table VII.—Straight Conductor; D = 0.5 cm.; d = 0.01 cm.;  $f = 5 \times 10^5$ .

æ.	$A = R/R_o$ .	B and Ref Reco.	$C = R_{sf}/R_{so}$ .
0 .05	1.06	21 ·3	13.6
0.1	1 ·26	12.6	18 6
0.2	2 .05	10.2	13 .6
0.8	3 ·86	11 .2	13.6
0.5	7 .55	15 · 1	13.6

Table VIII.—Straight Conductor; d = 0.01 cm.;  $\alpha = 0.3$ ;  $f = 5 \times 10^6$ .

n.	D.	$\mathbf{A} = \mathbf{R}_f/\mathbf{R}_v.$	$B = R_f/R_{so}$ .	$\hat{\mathbf{C}} = \mathbf{R}_{sf}/\mathbf{R}_{so}$ .
30	em. 0 · 1	1 ·10	8 .65	2 .94
120	0.2	1 .88	4.59	5.62
300	0.32	1 .95	6 48	8 .74
7 <b>5</b> 0	0.5	3 .36	11 .2	13 .65
8000	1.0	10.5	34.8	27 .15

Table IX.—Straight Conductor; D = 0.5 cm.; d = 0.01 cm.;  $\alpha = 0.4$ ; n = 1000.

f.	$\mathbf{A} = \mathbf{R}_f / \mathbf{R}_o.$	$B = R_f/R_{ro}$ .	$C = R_{sf}/R_{so}$
106	17 ·8	44.5	19 ·2 ·
5 . 10 <sup>6</sup>	5 · 2	13	13 .6
2 .5 . 100	2 .05	5.1	9.75
10 <sup>5</sup>	1 .17	2.9	6 25
5 . 104	1 .04	2.6	4.5

From Table VII it is seen that for the conditions there assumed the best space-factor is 0.2, but the stranded is slightly superior to the solid conductor over a wide range of space-factors. Table VIII shows the stranded conductor to be inferior for both extreme values, viz., 30 and 3000 wires, but slightly better than the solid for intermediate values. Table IX shows how the superiority of the stranded conductor at low frequencies disappears as the frequency is raised.

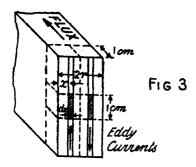
As an example of a type of stranded conductor largely employed, and of

the space-factor obtained, the following data are of interest:  $3 \times 3 \times 3 = 27$  wires each, No. 36 S.W.G. (d = 0.019), each wire single silk covered, and the whole double silk covered; D = 0.16 cm.;  $\alpha = 0.39$ . Tables III and VI show that this wire has a higher resistance than the solid wire which could replace it over the whole range of radio-telegraphic frequencies, with the possible exception of closely-wound solenoids at very long wave-lengths.

Strictly speaking, D should not include the insulation of the multiple conductor; this would give a somewhat larger value of  $\alpha$ , but would not modify the conclusions.

### PART II.

In the first part it was assumed that the distribution of the magnetic flux throughout the stranded conductor is not appreciably affected by the eddy-



currents in the individual wires. It is now to be seen whether this assumption is justified.

Fig. 3 shows a sectional view of a thin metal sheet, along which an alternating magnetic flux is maintained by some externally applied magneto-motive force. The thickness of the sheet is 2r, and a piece of the metal 1 cm. long and 1 cm. deep is indicated. If  $\delta\Phi$  is the magnetic

flux at any moment through the rectangular strip of width  $\delta x$  and length 1 cm, then the flux density B is  $\delta \Phi/\delta x$ , and the E.M.F. around the strip is  $-\frac{\partial}{\partial t}(\delta \Phi)10^{-8}$  volts. If the total upward electric force at a point in the metal is E,

$$\frac{\partial \mathbf{E}}{\partial x} = \frac{\partial \mathbf{B}}{\partial t} \cdot 10^{-8}$$
.

If the current density is  $\sigma$ , then  $\sigma = \frac{\mathbf{E}}{\rho}$  and  $\frac{\partial \sigma}{\partial x} = \frac{1}{\rho} \cdot \frac{\partial \mathbf{B}}{\partial t}$ .  $10^{-8}$ .

It is obvious from considerations of symmetry that the current distribution is the same on both sides of the centre line, along which  $\sigma$  is zero.

Let  $H_1$  be the applied magnetic force, assumed to be uniform over the whole cross-section, and let  $H_2$  be the magnetic force due to the currents in the plate; then as x increases to  $x+\delta x$ ,  $H_2$  will increase by an amount  $4\pi\sigma\delta x/10$ , and

$$\frac{\partial \mathbf{H_2}}{\partial x} = \frac{4\pi}{10} \, \sigma.$$

Since B = 
$$\mu$$
 (H<sub>1</sub>+H<sub>2</sub>),  $\frac{\partial B}{\partial x} = \mu \frac{\partial H^2}{\partial x} = \frac{4\pi}{10} \mu \sigma$ .

From the two formulæ

$$\frac{\partial \sigma}{\partial x} = \frac{1}{10^8 \rho} \cdot \frac{\partial B}{\partial t}$$
 and  $\frac{\partial B}{\partial x} = \frac{4\pi}{10} \mu \sigma$ ,

it follows that

$$\frac{\partial^{9} \mathbf{B}}{\partial x^{2}} = a_{1}^{2} \frac{\partial \mathbf{B}}{\partial t} \quad \text{and} \quad \frac{\partial^{2} \sigma}{\partial x^{2}} = a_{1}^{2} \frac{\partial \sigma}{\partial t},$$

where

$$a_1^2 = \frac{4\pi\mu}{10^9\rho}.$$

Assuming a sine law or simple harmonic variation with respect to the time, and adopting symbolic notation

$$\frac{\partial \mathbf{B}}{\partial t} = j\omega \mathbf{B}$$
 and  $\frac{\partial \sigma}{\partial t} = j\omega \sigma$ ,

and the above equations may be written

$$\frac{\partial^2 \mathbf{B}}{\partial x^2} = a^2 \mathbf{B}$$
 and  $\frac{\partial^2 \sigma}{\partial x^2} = a^2 \sigma$ , (15)

where

$$a^2 = j\omega \, \frac{4\pi\mu}{10^9 \rho}.$$

B and  $\sigma$  are now vector or complex quantities and to find the actual value at any moment, it is necessary to find the vertical component of the vector, or the imaginary part of the complex quantity.

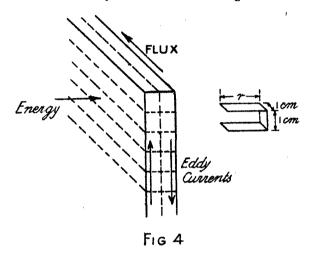
Putting 
$$a = \beta + j\alpha'$$
, we find  $\alpha' = \beta = 2\pi \sqrt{(f\mu/10^9\rho)}$ .

Equations (15) are identical with those found for the distribution of B and  $\sigma$  in the conductor when two flat parallel strips serve as the leads in an alternate current transmission. By solving equation (15) it can easily be shown that, if the frequency is very high, or the plate so thick that the penetration is small,  $\sigma = \sigma_1 e^{-\beta x}$ , where  $\sigma_1$  is the current density at the surface from which the depth x is measured; similarly  $B = B_1 e^{-\beta x}$ , where  $B_1 = \mu H_1$ , since at the surface  $H_2$  is zero and the resultant magnetic force H is equal to the applied force  $H_1$ .

All the energy dissipated within the plate is transmitted normally into it from the two surfaces and can be calculated by finding the energy entering each square centimetre of the surface, without any consideration of the distribution of current within the plate. It is interesting to note that the

<sup>\*</sup> In Part II, up to the adoption of symbolic notation in equation (15), the symbols H, B, and s, represent instantaneous values.

currents and losses within the plate would not be affected in any way by splitting the plate into two of half the thickness, and inserting between the two halves a very thin sheet of infinitely good conducting material. Similarly thin layers of infinitely good conducting material could be embedded at distances of 1 cm. as shown by the dotted lines in fig. 4. Now these fictitious



partitions form absolutely impenetrable reflectors of electromagnetic energy, and all the energy dissipated in each compartment must therefore have been . transmitted into it from the surface. This transmission of energy into and through the metal plate is governed by the same laws as the transmission of energy through air or other dielectric in the case of a telephone line or alternate current power transmission system, and may be calculated directly by the usual transmission line formulæ. The "transmission line" into each compartment of the metal sheet is of length r, i.e., half the thickness of the plate; it is short-circuited at the far end, viz., at the middle of the plate; its conductors, being of infinitely good conducting material, have no resistance, and its "dielectric," or, rather, the material through which the energy is transmitted, is copper or iron or other metal of which the plate may be made. The actual eddy-currents in the plate are the leakage currents of the fictitious transmission line. Considering a width of 1 cm. in the direction of the flux, as shown in the small sketch in fig. 4, the inductance L per centimetre of length of line, i.e. of penetration, is  $4\pi\mu/10^9$  henries, and the leakage G is  $1/\rho$ .

For a line of length r, short-circuited at the receiving end,

$$i_s = i_r \cosh ar$$
 and  $V_s = i_r \sqrt{(Z/Y)} \sinh ar$ ,

where the suffixes s and r refer to the sending and receiving ends respectively,

and Z and Y are the impedance and admittance per unit length of the line. The sending end impedance of the line

$$= \frac{\mathbf{V}_s}{i_s} = \sqrt{\frac{\mathbf{Z}}{\mathbf{Y}}} \tanh ar.$$

If P is the power supplied to the line

$$P = \frac{i_4^2}{2} \times \text{(real part of the sending end impedance)}.$$

In the present case 
$$\sqrt{(Z/Y)} = \sqrt{(j\omega L/G)} = \sqrt{(4\pi\omega\rho\mu 10^{-4})|45^{\circ}}$$
,  
=  $\sqrt{2\beta\rho|45^{\circ}}$ ,

and

$$\tanh ar = \sqrt{\frac{\cosh 2\beta r - \cos 2\beta r}{\cosh 2\beta r + \cos 2\beta r}} | \phi - \theta,$$

where  $\tan \phi = \tan \beta r / \tanh \beta r$  and  $\tan \theta = \tan \beta r$ .  $\tanh \beta r$ .

Hence the sending end impedance of the line

$$= \sqrt{2\beta\rho} \sqrt{\frac{\cosh 2\beta r - \cos 2\beta r}{\cosh 2\beta r + \cos 2\beta r}} |\phi - \theta + 45^{\circ}|,$$

and since

$$\cos(\phi - \theta + 45^{\circ}) = \frac{1}{\sqrt{2}} \cdot \frac{\sinh 2\beta r - \sin 2\beta r}{\sqrt{(\sinh^2 2\beta r + \sin^2 2\beta r)}},$$

$$P = \frac{i_s^2}{2} \cdot \beta \rho F(\beta t),$$

where t = 2r = thickness of the sheet, and

$$F(\beta t) = \frac{\cosh \beta t - \cos \beta t}{\cosh \beta t + \cos \beta t} \cdot \frac{\sinh \beta t - \sin \beta t}{\sqrt{(\sinh^2 \beta t + \sin^2 \beta t)}}$$

Introducing the field strength  $H_1$  at the outer face, instead of the fictitious line current  $i_s$ , since

$$H_1 = 4\pi i_s/10,$$

$$P = \frac{H_1^2}{2} \cdot \left(\frac{10}{4\pi}\right)^2 \beta \rho F(\beta t)$$
 watts,

where H<sub>1</sub> is the maximum value of the applied magnetic force.

This is the power transmitted into and dissipated within a column of the material of 1 sq. cm. cross-section, and of length r or t/2. This is equivalent to

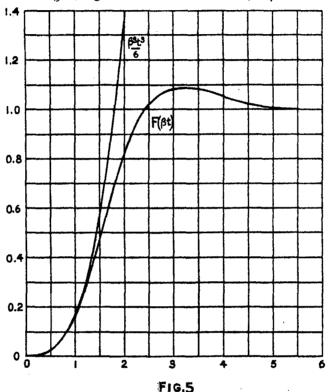
$$P = H_1^2 \left(\frac{10}{4\pi}\right)^2 \cdot \frac{\beta \rho}{t} \cdot F(\beta t) \text{ watts per cubic centimetre.}$$
 (16)

If  $\beta t$  is so small that all powers above the cube can be neglected,  $F(\beta t) = \beta^3 t^3/6$ , and

$$P = \frac{H_1^2 \omega^2 \mu^2 t^2}{\rho \cdot 24 \cdot 10^{16}}$$
 watts per cubic centimetre.

This agrees exactly with the value obtained directly on the assumption that the magnetic field is not appreciably affected by the eddy currents.

This approximate value of  $F(\beta t)$  can only be used if  $\beta t$  is small; for  $\beta t = 1$  it is 4 per cent. too high.  $F(\beta t)$  has been calculated, and the results plotted in fig. 5, together with the values of  $\beta^3 t^3/6$ .



If, instead of a continuous plate, there are a number of equally spaced rectangular rods, as shown in fig. 6(a), the path of the flux is successively through metal and air, but if the air spaces are narrow, the paths of the lines of force will not deviate appreciably from straight parallel lines, as shown in fig. 6(b). With round wires, which are, of course, always employed, and with a low space-factor, the flux distribution will be somewhat as shown in fig. 6(c). It is assumed, however, for the purposes of calculation, that the round wires are replaced by square ones of equal cross-section, and that the flux is as shown in fig. 6(b). On this assumption the only effect of the air spaces will be to cause a deeper penetration of the flux into the metal. If

$$\frac{\text{path of flux in metal}}{\text{total length of path}} = \psi,$$

then,  $H_1 = 4\pi i_i \psi/10$ , where  $i_i$  is the fictitious line current per centimetre width of conductor. This is equivalent to decreasing the permeability from

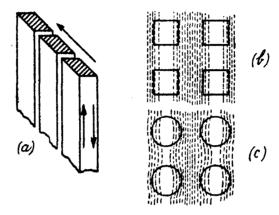


FIG 6

1 to  $\psi$ , in that it decreases the value of L in this ratio if the permeability of the metal is unity; if it is  $\mu$ , the equivalent reduced value is  $\mu\psi/(\psi+\mu-\mu\psi)$ . With this modification the formulæ for the continuous sheet can be employed and the air spaces neglected.

Assuming in what follows that the metal is non-magnetic,  $\beta$  will be replaced by  $\beta \checkmark \psi$ , and the power dissipated in the metal will be

$$H_{1}^{2}\left(\frac{10}{4\pi}\right)^{3}\frac{\beta\rho\sqrt{\psi}}{t\psi^{2}}F\left(\beta t\sqrt{\psi}\right)$$
 watts per cubic centimetre. (17)

If the conductors are square in cross-section and uniformly spaced, as shown in figs. 7(a) or 7(b), the space-factor  $\alpha = \psi^2$ , and if the cross-section of each wire is  $t^2$ , the power dissipated per centimetre length of each wire

490

If the wires are spaced as shown in fig. 7 (c),  $\alpha = 2\psi^2$ , and the power dissipated

= 
$$1.68 \,\mathrm{H_{1}^2} \left(\frac{10}{4\pi}\right)^2 \frac{\beta \rho t}{\alpha}$$
.  $\alpha^{1/4} \,\mathrm{F}\left(\frac{\beta t \alpha^{1/4}}{1.19}\right)$  watts per centimetre of wire. (18a)

To find the average value of the loss due to eddy-currents in a straight stranded conductor of circular cross-section carrying an alternating current with a maximum value of I amperes, it is necessary to substitute for  $H_1^s$  its average value throughout the whole cross-section. This has already been shown to be

$$41^2/50D^2$$
 (see equation 2).

The average loss due to eddy-currents per centimetre of individual wire, assuming equation 18,

$$=\frac{4}{50}\cdot\left(\frac{10}{4\pi}\right)^2\cdot\frac{\mathbf{I}^2}{\mathbf{D}^2}\cdot\frac{\beta\rho t}{\alpha}\cdot\alpha^{1/4}\,\mathbf{F}\left(\beta t\alpha^{1/4}\right)\,\mathrm{watts}.$$

The loss due to the main current I/n per centimetre of individual wire

$$=rac{\Gamma^2}{2n^2}\cdotrac{
ho}{t^2}$$
 watts,

and therefore the total loss per centimetre of individual wire

$$=\frac{\mathrm{I}^2}{2n^2}\left[\frac{\rho}{t^2}+\frac{n^2}{\pi^2\mathrm{D}^2}\cdot\frac{\beta\rho t}{\alpha}\cdot\alpha^{1/4}\mathrm{F}(\beta t\alpha^{1/4})\right].$$

Hence

$$R_f/R_o = 1 + \frac{n\beta t}{4\pi} \cdot \alpha^{1/4} F(\beta t \alpha^{1/4}),$$

or, substituting for  $\beta$ ,

$$R_f/R_o = 1 + \frac{nt}{2} \sqrt{\left(\frac{f}{10^9 \rho}\right)} \cdot \alpha^{1/4} F(\beta t \alpha^{1/4}). \tag{19}$$

For values of  $\beta t a^{1/4}$  less than unity, the approximate value, viz.  $F(x) = x^3/6$ , can be substituted; in this case

$$R_f/R_o = 1 + \frac{nt}{2} \sqrt{\left(\frac{f}{10^9 \rho}\right) \alpha^{1/4} \beta^{3} t^3 \alpha^{3/4}},$$
  
=  $1 + \frac{n\alpha t^4 \beta^4}{24\pi}.$ 

For copper  $\rho = 1.7 \cdot 10^{-6}$  and

$$R_f/R_o = 1 + 7.15 \cdot 10^{-6} n_f^2 t^4 \alpha$$
.

Substituting round wires of diameter d of equal cross-sectional area for the square wires of side t, so that

$$\pi d^2/4 = t^2,$$
 $R_f/R_o = 1 + 4.4 \cdot 10^{-6} n f^2 d^4 \alpha,$  (20)

which agrees with the value calculated in Part I, equation (3a), except that the constant was there found to be 4.2.

In a single-layer solenoid, wound with S turns per centimetre of a stranded conductor of square cross-section with side  $\tau$ , the average value of  $H_1^2$  over the cross-section has been shown to be

$$\frac{16\pi^2 I^2 S^2}{300}$$
 (see equation 4).

Substituting this value of H<sub>1</sub><sup>2</sup>, the loss due to eddy-currents in each individual wire

= 
$$\frac{I^2S^2\beta\rho t}{3\alpha} \alpha^{1/4} F(\beta t\alpha^{1/4})$$
 watts per centimetre,

whilst the loss due to the main current of I/n is

$$\frac{\mathrm{I}^2}{2n^2}\,\frac{\rho}{t^2}.$$

Hence, putting  $nt^2 = a\tau^2$ , we have

$$R_c/R_o = 1 + \frac{2}{3} (S\tau)^3 n \beta t \alpha^{1/4} F(\beta t \alpha^{1/4}),$$

or, substituting for B,

$$R_c/R_o = 1 + \frac{4\pi}{3} (S\tau)^2 nt \sqrt{\left(\frac{f}{10^6 \rho}\right)} \alpha^{1/4} F(\beta t \alpha^{1/4}). \tag{21}$$

For values of  $\beta t \alpha^{1/4}$  less than unity this becomes

$$R_c/R_o = 1 + \frac{1}{8} (S\tau)^2 nat^4 \beta^4$$

For copper this reduces to

$$R_c/R_o = 1 + 59.4 \cdot 10^{-6} \cdot n f^2 t^4 \alpha (S\tau)^2$$

or, substituting round wires of equal cross-section,

$$R_c/R_o = 1 + 36.7 \cdot 10^{-6} \cdot n f^2 d^4 \alpha (S\tau)^2,$$
 (22)

which agrees with the value found in Part I, equation 5b, except that the constant was there found to be 35.6.

Equations 20 and 22 are independent of any assumption as to the arrangement of the wires, and can be obtained either from equation 18 or 18a.

Hence the method adopted in Part I is permissible, and the values given in Tables I-VI are correct for values of  $\beta t \alpha^{1/4}$  less than unity. For copper,  $\beta = 0.152 \sqrt{f}$ , and, assuming  $\alpha = 0.5$ , t must not exceed  $7.9 \sqrt{f}$ . If round wires of diameter d are substituted for square wires of side t, their cross-sections being equal, the largest sizes of wires at various frequencies, for which the method of Part I is applicable, are as follows:—

$$f = 10^6$$
, 5.10<sup>5</sup>, 2.5.10<sup>5</sup>, 10<sup>5</sup>, 5.10<sup>4</sup>,  $d = 0.009$ , 0.013, 0.018, 0.028, 0.04 cm.

For smaller values of a than 0.5, the limiting values of d can be further Hence Tables I, II, IV, and V can be relied upon at all frequencies, and Tables III and VI at frequencies below 2.105, i.e. for wave-lengths exceeding 1500 metres. It is only with the largest wire, viz., d = 0.02 cm., at the higher frequencies, that the screening action of the eddy-currents causes an appreciable diminution in the eddy-current losses, and gives values of R<sub>f</sub>/R<sub>o</sub> or R<sub>c</sub>/R<sub>o</sub> smaller than those given in the Tables. A comparison of the columns headed B and C for  $f = 10^6$  shows, however, that, even if the high-frequency resistance of the stranded conductor were reduced to half the value there given, it would still offer no advantage over the solid wire which could replace it. An accurate calculation of the first example in Table III gives  $R_f/R_g = 1.66$  instead of 2. If the accurate formula involving  $F(\beta t\alpha^{1/4})$  is used to determine the best value of the space factor, the results obtained differ very little from those given in the Tables.

In establishing the various formulæ in this paper, it has been tacitly assumed that each individual wire is situated in a uniform magnetic field, except for the effects of the eddy-currents in the wire. This is not strictly true, since the field increases in intensity with increasing distance from the centre in the case of a straight conductor, and with increasing distance from the outer surface in the case of a solenoid. This introduces a dissymmetry in the distribution of the eddy-currents within each wire, and thereby increases the losses and the high-frequency resistance. attempt to take this secondary effect into account would greatly complicate the equations, and is thought unnecessary.

## On Permanent Periodicity in Sunspots.

By Sir JOSEPH LARMOR, F.R.S., Cambridge, and N. YAMAGA, University of Tokio.

(Received March 28, 1917.)

The most important index to the dynamical constitution of the Sun lies in its dark spots, which have been known, ever since their discovery by Galileo, to recur periodically. Numerical data for the numbers of spots simultaneously present, and later and more precise data for the extent of spotted area, are in existence for about two centuries; and it is natural that efforts should be made, from all points of view, to extract the knowledge which they contain.

The discussion of the fundamental question, whether there is permanent unbroken periodicity, due either to planetary influence or (as seems much more probable) to a period of dynamical oscillation belonging to the Sun itself, was taken up statistically by Dr. Simon Newcomb in a paper "On the Period of the Solar Spots." His criterion was to examine whether the more precise phases were equidistant throughout the record, or on the other hand their deviations increased continually (as  $\sqrt{n}$ ) according to the law of errors. The phases chosen for scrutiny were four, those of maxima and minima and the two more definite intermediate times of mean spottedness. An analysis by the method of least squares led him to an unbroken period, of  $11.13 \pm 0.02$  years, and thus of great definiteness. His conclusion is that "underlying the periodic variations of spot activity there is a uniform cycle unchanging from time to time and determining the general mean of the activity." But to get this very remarkable degree of precision he had to reject the records belonging to the two decades around the year 1780, which showed violent irregularity in the phases. "I was at first disposed to think that these perturbations of the period might be real, but on more mature consideration I think they are to be regarded as errors arising from imperfection of the record. derivation of any exact epoch requires a fairly continuous series of derivations made on a uniform plan. If we compare and combine the results of observations made in an irregular or sporadic way, it may well be that the actual changes are masked by the apparent changes due only to these imperfections." And, again, "it would seem from what precedes that a revision of the conclusions to be drawn from the observations of sunspots during the interval of 1775-1790 is very desirable."

In the graphical analysis which follows, we shall be driven to reject the

<sup>\* &#</sup>x27;Astrophysical Journal,' vol. 13, pp. 1-14 (1901).

record of the two cycles of the spots, here referred to, for much more conspicuous and emphatic reasons; so violent a temporary interruption as they show, in the course of a phenomenon periodic in phase and on so vast a scale, seems to be most anomalous. It is true that the graph (fig. 1) shows shrinkage in numbers of spots recorded in not a few cycles, involving change of ordinate smaller indeed but yet of the same order of magnitude as the discrepancy in those two cycles; but in no other case is the period deranged. All the rest of the graph is consistent with a law represented by the product

$$\phi(t) \mathbf{F}(t)$$
,

where F(t) is a function strictly periodic in  $11\frac{1}{8}$  years, and  $\phi(t)$  is a slowly changing factor (cf. fig. 9) which determines the varying amplitude.

The next analytical discussion is a memoir by Prof. Schuster, "On the Periodicity of Sunspots," which applied the method of quasi-optical analysis elaborated by him, in order to determine the periodogram of the disturbance. viz., the curve connecting amplitude with frequency in the continuous range of simple undulations into which the data for a specified range of time, taken by themselves, can be analysed. This memoir is the most complete and important analysis that has yet been made, and the data marshalled in it from Wolf and Wolfer, and from the records of Greenwich and of the Solar Physics Observatory, have been largely employed in the present discussion, The very striking, even at first sight startling, result is reached by him, that when the data for the last available 150 years are divided into two equal groups, their periodograms come out totally different; the more recent group showing a nearly pure simple undulation of Newcomb's period 114 years, while the earlier group hardly shows this period at all, but exhibits prominently two somewhat broad and indefinite periods of about 134 and 94 years. Yet Prof. Schuster also assigns much weight to Newcomb's feature, that the turning points and mean points on the graph of spot-frequency occur at equidistant times throughout the range, except for the one conspicuous but transient local disturbance after which the phases recover the previous sequence; he considers that this is strong evidence that the 11½-year period thence predicted is a permanent property over the whole range, and of some sort of dynamical type. One of the chief points elucidated in the present more elementary and direct discussion is the cause of the disappearance of this period of 11½ years on the analysis of the record from 1750 to 1820. It is that the two spot-cycles, already referred to, between 1776 and 1798, which are conspicuous and therefore greatly influence the analysis, are entirely abnormal. If this range of the data is left out, the rest of the

<sup>\* &#</sup>x27;Phil. Trans.,' February, 1906.

record falls in satisfactorily with a permanent 11½-year period. This is brought out especially by the graphs which show, superimposed, the forms of the periodic components having this period, that have been extracted from the three ranges separately into which the record has been divided for the purpose of this test.

More recently, Prof. Kimura\* has obtained, by a process of adaptation, a series of trains of unlimited simple undulations which closely represent the sunspot graph over the 164 years of available record, represented here in A free curve drawn through the ordinates representing these discrete amplitudes, ranged at equi-distant frequencies, would trend towards being a periodogram. In two following papers, Prof. H. H. Turner has pointed out that this group of components coincides closely with the Fourier series representing this record of the 164 years, repeated, however, without This coincidence is not a physically necessary one, for the Fourier components determined from a longer range would, of course, include this range, not however repeated in the same manner. And the periodogram curve will not be the same either, unless the original material is homogeneous, in a statistical sense of which such identity would be the Prof. Turner points out that the presence of a periodicity strongly sustained over a considerable length of the data, but not identical with one of these Fourier harmonics, would tend to be revealed by abrupt change of sign in the range of amplitudes; and he shows how the value of this period might be deduced, provided, however, it belongs to an unending simple train.

The number of spots is necessarily positive; but, as it fades to zero as well as rises to a maximum, it may be held to be a measure of the energy of the solar disturbance, which is proportional to the square of an amplitude purely alternating from positive to negative, in the simplest case say to  $\cos^2 pt$ , which is  $\frac{1}{4} + \frac{1}{4} \cos 2pt$ , representing oscillation around a mean.

At first glance, this view may not be quite in keeping with the antisymmetrical character (infra) of the periodic part of the graph, which rather indicates a mean spottedness with this special type of periodic fluctuation superimposed on it; this other special feature, that the total spottedness falls sensibly to zero at the minimum before rising again, must also be kept in view

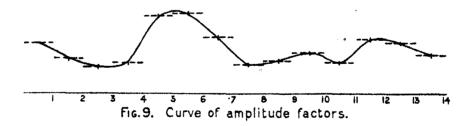
The very fundamental character of the solar phenomena that must be concerned in the spots will justify the application of a direct method, involving perhaps fresh features and principles, to this well-worn problem. A considerable selection from our graphical representations has been here

<sup>\* &#</sup>x27;M. N. Roy. Astron. Soc., May, 1913.

included, as the inferences rest more on visual inspection than on calculation; and, moreover, experience has shown us that it will be convenient for inquirers who in future approach the subject, to have ready at hand the graphs which constitute the material of the problem.

The graph given in fig. 1 represents the sunspot record, year by year, from 1750 to 1914, the data for the last years from the Greenwich record having now been added to the numbers as tabulated by Dr. Wolfer and the areas as recorded by the Solar Physics Committee and at Greenwich up to 1902, which are the data that have been discussed by Newcomb and by Schuster. Each ordinate in the graph is the mean of three consecutive monthly records, so as to give a mean record all round the Sun instead of mainly on one hemisphere. The broken arrows mark off the Wolfer-Newcomb-Schuster cycles of 11:13 years; the full arrows represent an altered trial period of 11:21 years, which perhaps fits more obviously with the phases of the most recent data. In any case it will be of utility to have analyses for two trial periods. The misfit of both sets of arrows between 1776 and 1798 is obvious. A smooth mean curve has been drawn through the jagged peaks of the numerical data in fig. 1.

The discussions of Wolfer, Newcomb, and Schuster having afforded strong evidence for a very definite secular periodicity unbroken as regards phase, its varying amplitude in the sunspot graph still remains for consideration. The procedure employed here is to multiply the amplitudes throughout each cycle by a common factor, so that all the cycles shall become equal in mean amplitude. The result is represented in fig. 2; the multipliers required to deduce fig. 2 from fig. 1 are represented, smoothed out into a curve  $\chi(t)$ , in fig. 9, in which each short line represents the actual constant multiplier for a



cycle. If  $\psi(t)$  represents fig. 2, and f(t) represents fig. 1, which is the actual sunspot graph, then

$$f(t) = \chi(t)^{-1} \cdot \psi(t).$$

The curve of  $\chi(t)$  in fig. 9 shows that this amplitude factor  $\chi(t)$  changes gradually throughout the whole range of the data. Thus, if we assume that

the  $11\frac{1}{8}$ -year constituent F(t) of the sunspot record is of constant period but varying amplitude, it will be represented with fair fidelity by

$$\chi(t)^{-1}\Psi(t)$$
,

where  $\Psi(t)$  is the periodic constituent of this period that is involved in the modified graph  $\psi(t)$  of fig. 2.

The method of extracting a secular constituent of unbroken period  $\tau$  from a graph is (figuratively) to wrap the graph round a cylinder whose circumference is  $\tau$ , and take the mean ordinates of the various convolutions to form a new curve. All elements of an undulating graph which have not a period at  $\tau$ , or near it, will then average out; if the range of the graph that is utilised is a large multiple of  $\tau$ , the result may be presumed to represent with fidelity the periodic constituent required. This periodic part, of form thus isolated, may then be analysed into a Fourier series representing the fundamental simple period  $\tau$  and its submultiples.

It will readily appear, on consideration of the nature of this process, that the values of these simple harmonic periods of equidistant frequencies, thus determined, will agree with the ordinates in a continuous periodogram\* which represents the actual disturbance over the long range that is thus analysed, taken, however, by itself, with nothing added outside that range. But we are now dealing, by hypothesis, with the different case of a definite period repeating itself outside that range as well as inside; its components will represent unbroken periods, and the periodogram for them will be, strictly, a series of isolated narrow peaks with vanishing intermediate amplitudes; if the rule is retained that the amplitude of a component of range  $\delta n$  is the element of area of the periodogram, these isolated ordinates would have to be infinite in length. The continuous periodogram curve thus cannot quite naturally represent sharp permanent periodicities, and a different procedure as here, in fact a much simpler one, is as regards them to be preferred.

On the other hand, the periodogram analysis, as elaborated by Prof. Schuster, is well adapted to the discussion of material containing transient periodicities repeated irregularly, but with the same periods, or tendencies to periods, recurring. The standard example is natural radiation. If two reaches of the material that is analysed, of sufficient lengths, lead to like periodograms, then to that degree the material may be presumed to be statistically homogeneous; otherwise it is fortuitous and sporadic. It seems to be inferable from Prof. Schuster's analysis that the sunspot record, apart from the 11½-year

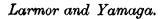
<sup>\*</sup> With amplitude plotted against frequency, not length of wave.

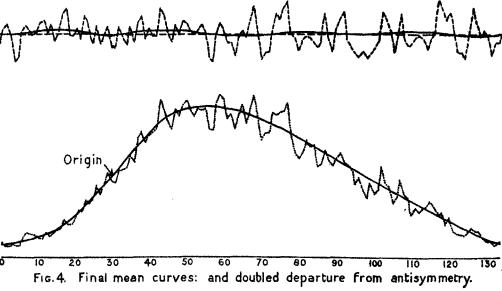
period, is in the latter category." Yet it is at first sight startling that the 111-year period is almost non-existent in the periodogram of the first of the two 75-year ranges; for, although that range contains two anomalous cycles of 22 years, the other cycles are normal, and might be expected to show in the result. But such destructive interference is really not anomalous. For example, if a range of length L contain a train  $A\cos(nt+\alpha)$ , limited to length l which is a considerable number of periods, this train will, irrespective of its position along the range, add to the periodogram at its own period a term approximately l/L. A (cos  $nt + \alpha$ ), exhibiting there a maximum ordinate lA/L of phase a. If the range contain a number of such limited trains of uniform amplitude, their contributions can be summed by the vectorial graphical process into a single term  $A'\cos(nt+\alpha')$ . there are many of them, and their phases a are sporadically distributed, the resultant of their vector amplitudes will be very small compared with the arithmetic sum, and will often be quite insensible. But if we include a succession of very many such ranges L, and the phases a of the component trains vary sporadically all along, then, by Lord Rayleigh's principle, the total resultant amplitude has a sharply defined probable value, equal to the most probable value for a single range, multiplied by the square root of the number of ranges, a value, in fact, determined from the total energy along the range, treated as additive. The optical analysis of radiation is an average, then, rendered definite by ranging over an extremely great number of periods; we can, in general, expect nothing so definite, unless under exceptional circumstances, for shorter ranges of graphs, such as are alone available in observational material or amenable to Fourier analysis.

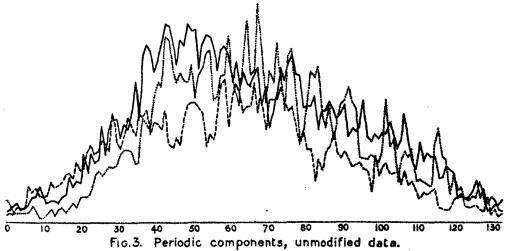
The constituent of period 1113 years, as determined from the monthly sunspot numbers graphed in fig. 1, by this procedure of superposition of periodic lengths, conducted arithmetically (but modified by omission as infra), is represented in fig. 3 and fig. 4. The process has been arranged so as to provide a test for the hypothesis of unbroken periodicity, by dividing the range of the data into three nearly equal parts, extracting the graph of the periodic constituent from each of them, and taking the mean of these three graphs superimposed in fig. 3, duly weighted if necessary, for the final result in fig. 4. The more nearly concordant these partial graphs in fig. 3 turn out to be, the more justified is this hypothesis as against sporadic broken periods. The roughest trial shows, however, at once that this hypothesis, otherwise quite satisfactory, is wholly upset in the two abnormal and

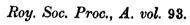
<sup>\*</sup> On this general subject, see Sir J. Larmor "On the Fourier Harmonic Analysis," in Presidential Address, 'Proc. Lond. Math. Soc.,' pp. 8-42, November 2, 1916.

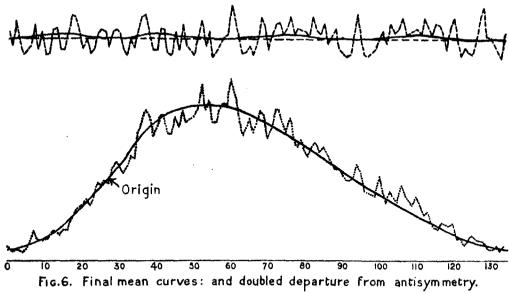
<sup>†</sup> Cf. loc. cit., 'Proc. Lond. Math. Soc.,' p. 35, November, 1916.

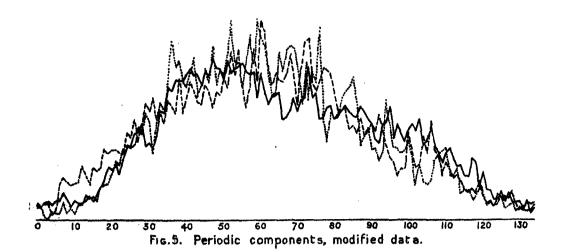












conspicuous cycles shown in fig. 1 between 1776 and 1798. The course very strongly suggested is to omit them from the data to be analysed, as for some reason wholly foreign to the problem; this will in no way affect the validity of the analyses of the rest of the sunspot graph, but the question will remain over, whether there has been error of record or whether some overmastering transient cause has completely masked the normal run of the data. When the magnitude and the time-scale of the solar phenomena that are involved is borne in mind, the former alternative seems to be the preferable one; it was the one adopted by Newcomb for reasons quoted supra.\*

The two sunspot cycles from 1776 to 1798 have been accordingly omitted and the remainder of the data divided into three groups of nearly equal duration:

```
(----) 1750 to 1822, omitting 1776 to 1798, (-----) 1822 to 1867, (.....) 1867 to 1912.
```

The constituents of period 11·13 years extracted from these groups of the original data (fig. 1) are recorded in fig. 3, that from the first group being represented by the broken line, that from the second by the continuous line, and that from the third by the dotted line, as indicated above along-side the ranges of time. It will be seen that these three graphs do fairly superpose;† the fact that this coincidence is not very good, even when allowance is made for the small number of cycles in each group, arises

<sup>\*</sup> In reply to inquiry as to whether the records could possibly be so greatly in error for these two cycles, Prof. Wolfer has kindly referred us to his classical memoir in the Zürich 'Vierteljahrsschrift,' 1902, where in pp. 80 seg. he discusses the discrepancies between the various early records; nothing, however, so substantial as is here in question seems to emerge. At the end, p. 95, Prof. Wolfer recalculates the 11-year period and its epoch, obtaining a result (11'124 ± 0'030 for the period) in close agreement with Newcomb's then recent one, notwithstanding variations in detail of the data employed, and substantially in agreement with earlier determinations by Wolf and Sporer, and by himself in 1892. Prof. Wolfer has also constructed a graphical representation, like fig. 1 here, on a very open scale, for the whole range from 1750 ('Zürich Astr. Mitteil.,' vol. 93; 'Monthly Weather Review,' April, 1902), which does not any more than fig. 1 give ground for the suggestion of faulty records, whatever may he said as to the minor matter, from the point of view of our present discussion, of indetermination of the principal phases. Reference should also be made to the 'Meteorolog. Zeitschrift,' vol. 5, 1915, where Prof. Wolfer arranges the sunspot data for the interval 1901-1914. Earlier knowledge of these references would have facilitated and probably improved our present discussion; but the main issues that arise in it are on a large scale, and would not be sensibly affected by change in the details of presentation. [See addition, p. 503, infra.]

<sup>+</sup> The steep rise and gradual fall is a well known feature of each cycle separately.

mainly from the presence of low amplitudes in a range of the cycles (1800–1834) mostly in the first. The (unweighted) mean of the curves for the three groups, which represents the whole of the data, is recorded in fig. 4, both as a broken graph representing the actual numerical record, and as a smoothed curve such as a physical periodic constituent would naturally be. It will be observed that the smooth curve is here a good representation of the broken graph; and this is in part because the cycles of low amplitudes are now swamped by the greater number of cycles with amplitudes more normal.

We have also extracted, for comparison, the periodic part from fig. 2 in which the amplitudes of the cycles have been equalised. The results are shown in fig. 5 and fig. 6. The three constituent ranges in fig. 5 now agree much more closely; but their mean, fig. 6, differs little from the previous form, fig. 4, for a reason already assigned. In the two latter curves (fig. 5 and fig. 6), the period has been taken as 11:21 years (somewhat at random, cf. p. 496) instead of 11:13, as was to be anticipated (p. 501 infra); this slight change of period does not sensibly affect the form of the periodic constituent, and it is unnecessary to exhibit graphs for both periods.

The Fourier analysis of the periodic part of the unmodified sunspot curve thus extracted, is, in arbitrary units,

 $44.5 + 35.4 \sin kt + 6.6 \sin 2kt$ 

and of the same curve modified to equal amplitude is

 $45 + 37.8 \sin k't + 6.5 \sin 2k't + 1.4 \sin 3k't$ 

where the periods chosen are  $2\pi/k$ , or 11·13 years, and  $2\pi/k'$ , or 11·21 years. Terms in the series with amplitude less than unity are omitted, as being within the limits of uncertainty. With this limitation, no cosines appear in the expressions. Thus, when the origin is taken on the periodic curve at middle height, that curve is of type satisfying the relation F(-t) = -F(t), the positive side of it being the reversed image of the negative side.

As this antisymmetrical character is remarkable, and probably suggestive for physical theory, we have confirmed it by constructing a graph of each of these Fourier series and fitting these graphs on to the original curves from which they were derived. Nowhere is the discordance more than one-thirteenth of the maximum ordinate, and that amount is very local; the curves are in the main so close that the difference would hardly show on diagrams of the size here given.

The antisymmetrical character of the periodic graph that is thus revealed may also be scrutinised directly, without the analysis into Fourier components. Any graph whatever G(t) can be divided into a symmetrical part  $\phi(t)$  and an

antisymmetrical part f(t) with respect to any origin, these even and odd functions being determined by the equations

$$G(t) = \phi(t) + f(t), \qquad G(-t) = \phi(t) - f(t).$$

In the present case the symmetrical component, equal to  $\frac{1}{2}G(t)+\frac{1}{2}G(-t)$ , is at any rate small. Its value can be plotted by folding the periodic graph over on itself, and then marking the mean (half sum) of the two ordinates, one positive, one negative. The results thus obtained for the rugged graph representing directly the numerical data, and for the smoothed curve, are given by the two flat curves drawn above the periodic graphs in figs. 4 and 6, when the ordinates in them are reduced by halving. These curves, thus halved, by comparison of their ordinates with the irregularities that were smoothed out in the periodic graph, provide a criterion of the degree of certainty of the property now under discussion. If it is regarded as confirmed, a slightly purified value of the periodic graph itself would be given by  $\frac{1}{2}G(t) - \frac{1}{2}G(t-t)$ .

If figs. 3, 5, and 4, 6 are supposed shifted along into contact, each pair will represent roughly two waves of the period, and the lower bend of the curve may be seen by eye to be of the same form and size as the image of the upper bend.

We have yet to show that the process of reduplication of the graph, in order to extract permanent periodic components, can be relied on, *i.e.*, that the effect, on the periodic graph so obtained, of a small error  $\alpha$  in the true period  $\tau$  is negligible. If F(t) is the true periodic part of the graph, so that  $F(t+\tau) = F(t)$ , the use of a trial period  $\tau + \alpha$  will produce from the material instead of F(t), a quantity substantially equal to

$$F(t) + F(t+\alpha) + F(t+2\alpha) + ... + F(t+n-1 \cdot \alpha)$$

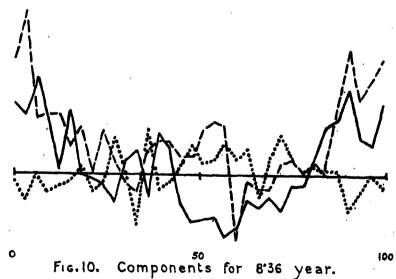
divided by n the number of reduplications or cycles in the data. As  $\alpha$  is small this is approximately

$$\frac{1}{n\alpha}\int_{t}^{t+n\alpha}\mathbf{F}(t)\,dt.$$

The ordinate as computed on the trial period  $\tau + \alpha$  is thus the mean value of the ordinate of the true periodic part over the range  $n\alpha$ , on the positive side of t when  $\alpha$  is positive. So long therefore as  $n\alpha$  is small compared with  $\tau$ , an error in the period will lead to but slight error in the form of the periodic component thence derived; for the presumption is that the true periodic part is represented by a smooth curve without violent bends. An illustration is afforded by the result of the trial periods 11·13 and 11·21 years in fig. 4 and fig. 6. Had their data been the same, instead of being fig. 1 and fig. 2, the criterion of direction of the error would have indicated that the latter may be

nearer the correct period. For the amplitude derived from a trial period will. be maximum when it coincides with the true period.

The question arises whether the constituent of period 111 years thus determined is the only continuously periodic element in the sunspot record. Other likely periods might be tested by the same process, but there is the disadvantage that periods commensurable (or nearly so) have a part in common, made up of their common harmonics,\* which may have to be separated out. It is more convenient and suggestive to take out from the record the periodic part already found and analyse the residue. The residue for the natural graph (fig. 1) is given in fig. 7, and that for the modified graph of equal amplitudes (fig. 2) is given in fig. 8. In these residues, the two defaulting cycles are, of course, conspicuous. The residue when the fundamental simple constituent alone of the 11g-year periodic part has been removed, is given as a graph in Prof. Schuster's memoir (p. 92), and the peaks that it reveals (mainly, however, in its first half, which contains the two abnormal cycles,-they would hardly be noticed in the second half by itself) suggest to him a possible permanent period of 8.36 years. residue, when the whole of the 11½-year period is removed, has been tested for this period by the same process as above, dividing up into three groups. The results are shown in fig. 10: that of the third group containing the most



modern and exact data undulates closely along the zero axis, and thus shows no such period; the first and second groups both show rises from the zero

\* In the optical analogy of spectroscopic analysis by a grating, this corresponds to the overlapping of spectra of different orders.

axis at the beginning and end, and thus have something in common; but when the two abnormal cycles are omitted, the first group gives a graph lying close along the axis, as did the third; the second result, thus remaining unsupported, is from its form most probably accidental. We thus find no indication of a permanent period near 8:36 years.

Our conclusion is that a secular unbroken solar periodicity of about 11½ years, controlling superficial solar phenomena, is established firmly, if we may omit from the record of 160 years the two strongly discrepant cycles from 1776 to 1798. We have found that the graph of this periodic constituent has the remarkable property of being antisymmetrical with respect to the axis which bisects its undulations, each undulation giving equal areas above and below and the curve repeating as an inverted image; which may contain a clue for a physical theory. We have found no indication that the residue of the sunspot activity, after this periodic part is removed, is of other than fortuitous sporadic character, not amenable to further analysis as a whole. This latter result is supported by the totally different characters of the periodograms found by Prof. Schuster for two successive ranges of 75 years, which favour the extended conclusion that the residue involves no sporadically repeated transient periodicities such as might arise from recurrent damped oscillations, as well as no unbroken secular periods.

[Added March 29.—We are permitted to append a letter from Dr. Wolfer, giving very important information as to the value of the data on which discussions like the present one depend. The uncertainty which he emphasises as to the units of measurement along the range of time, seems fully to justify our omission of the very widely discrepant interval, and also enhances the interest of the analysis of the data of fig. 2, in which the amplitudes of all the cycles have been artificially equalised. The customary mode of discussion, which includes epochs or phases alone, eliminates this uncertainty arising from varying scale; though, of course, individual epochs are liable to non-cumulative displacement by the residue of disturbance, especially when the cyclic amplitude is small. The results of a complete revised discussion of all available data, such as Dr. Wolfer promises, will be eagerly awaited.

"Eidgenössische Sternwarte, Zürich, March 19, 1917.

"In reply to your letter of March 14, I take pleasure in giving you some particulars about the sunspot statistics for the critical interval from 1775 to 1795, as far as they are at hand. This interval has always been and will remain a very unsatisfactory one, the spot observations during that time being very scanty, and depending almost exclusively on one single observer,

Staudacher, of Nuremberg. On the other hand, just for that reason, they are more homogeneous than many others of remote times, and fortunately they are somewhat more numerous at the time of maximum solar activity than for the minimum epochs, which seemed to be of little interest to the observer. Therefore, the epochs of spot maxima (1778 and 1787) as determined by Wolf are resting upon a tolerably good base, and their uncertainty does not exceed, probably does not even reach, a year. The large departures of the lengths of the periods observed between 1770 and 1805 from the mean value of 114 years are certainly to be considered as real, and could not be explained by the deficiency of the observations. It is not quite the same with regard to the amplitudes, or the relative heights of the different maxima of that time, especially those of 1778 and 1787. The numbers of spot frequency are, of course, much more influenced by the gaps in the observations, and it is impossible to get reliable monthly and yearly means from perhaps 20 or 30 observations scattered irregularly over the year. Another difficulty lies in the determination of the factors by which the spot numbers of different observers with different instruments are reduced to the same unit, to make them comparable inter se. This requires a continuous system of corresponding observations of the successive observers, beginning with Wolf-as normal observer and as unit-and extending backward as far as possible from later observers to former ones. Wolf, in his inaugural investigation, did not employ all the available corresponding observations for the evaluation of these factors, and it is probable that the factors are, in some cases, uncertain, and require corrections. For Staudacher, for instance, I consider it too large, and also for some other contemporary observers whose factors had to be deduced from that of Staudacher, like Oriani, on whose observations the maximum of 1778 is mainly depending. I believe the exceptionally high spot numbers of this maximum are partly due to this fact just mentioned. It will be felt in any investigation in spot periodicity founded upon the whole complex of spot numbers—the "relative numbers" instead of the epochs of maximum and minimum alone.

"A new reduction of the old observations, back to 1749, based on a new determination of the reduction factors, has been begun here several years ago, but it is a very big task, and has not yet far advanced."]

[Added April 30.—The meaning of the term sporadic, as employed above, may be more closely defined. The degree in which the quality described by that term is present varies inversely as the length on the graph within which there is some amount of correlation between the underlying causes; when a graph is highly sporadic, each small range of the curve is an

independent entity, practically in no relation to the adjacent ranges except that of statistical averages. In any attempt at harmonic analysis of such a graph we must therefore expand each short element of the graph into its own Fourier integral, and combine the results for all the elements as the laws of chance direct. Now, the Fourier integral for any duly limited graph  $\phi(x)$  is given by

$$\phi(x) = \int_0^\infty dn f(n) \cos nx + \int_0^\infty dn F(n) \sin nx,$$

where

$$f(n) = \frac{1}{\pi} \int_{-\infty}^{\infty} \phi(x) \cos nx \, dx, \qquad F(n) = \frac{1}{\pi} \int_{-\infty}^{\infty} \phi(x) \sin nx \, dx.$$

If  $\phi(x)$  represents a physically correlated constituent element of the graph, situated at the origin and of sensible value only very near the origin, of total area A, the formulæ approximate to

$$f(n) = \frac{1}{\pi} A, \qquad F(n) = 0.$$

Thus the local element of the graph, situated at the origin of x and of area A, is represented in its harmonic analysis by the integral

$$\frac{\mathbf{A}}{\pi} \int_0^\infty dn \cos nx.$$

All the ordinates in its periodogram for frequencies tend to equality, except for wave-lengths that are not long compared with the length of the element. This remark develops into the conclusion of Rayleigh and of Schuster that the periodogram of uncorrelated disturbance, or of any kind of disturbance as regards wave-lengths much beyond its range of correlation, would be a straight line, all periods being equally present. But such a conclusion implies that the area A of the local constituent element of the graph is not null. If that were so, and the disturbance were thus as much negative as positive, it would be representable by the gradient of some function which vanishes beyond the element, say by  $\phi'(x)$ ; its Fourier integral would thus be obtained from the previous expression by differentiation, in the form

$$-\frac{A}{\pi}\int dn\,n\sin\,nx.$$

The ordinate of the periodogram of amplitudes of an alternating disturbance would thus be proportional to the frequency, as regards components whose wave-length is long compared with the length of the elementary graph or with the range over which correlation holds in the complex disturbance. This agrees with the facts for natural radiation, which dynamically must be

constituted of such alternating pulses; the wave-length at which this law that intensity varies as  $\lambda^4T$  begins to assert itself affords a measure of the length on a ray over which correlation extends, viz. of the mean effective length of the constituent pulses in ordinary light.

Scrutiny of the variation of the intensity of Rubens' quartz Reststrahlen (1901) with temperature seems to indicate correlation extending sensibly over a range of about six wave-lengths of yellow light, for the case of these long waves at ordinary temperatures; but the formula of Planck with modern values of the constants, not specially adjusted for long waves, gives as much as eight times this range for natural radiation.

It would, of course, be possible for a graph, like the residual graph of sunspots, to be devoid of correlation over the short range that is available for scrutiny, though it would come in on a much coarser scale over a long range.]

The Lateral Vibrations of Bars of Variable Section.

By J. W. Nicholson, M.A., D.Sc., F.R.S., Professor of Mathematics in the University of London.

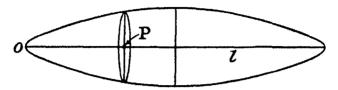
(Received May 11, 1917.)

The present investigation, though strictly mathematical in character, arose in connection with a suggestion, put forward by Prof. A. Dendy and the present author in another paper communicated to the Society,\* that the siliceous deposits found on certain sponge spicules occurred at nodes of the spicules, regarded as vibrating rods. These vibrations, being set up and maintained by the impact of currents of water on the spicules, are necessarily of the lateral type. For the detailed examination of such a suggestion, it is necessary to obtain a comprehensive account of the positions of the fundamental nodes on a free-free bar, as dependent on the law of variation of its cross-section. The present paper contains, in fact, the formal analysis whose results were quoted without proof in the other paper.

This analysis is of considerable generality, as will appear, and the particular examples selected for purposes of illustration, together with the manner in which the variable cross-section is dealt with, have been determined by the requirements of the biological application already mentioned. One general problem is in view throughout the work, and it may be stated as follows:—

<sup>\* &#</sup>x27;Roy. Soc. Proc.,' B, vol. 89, p. 573 (1917).

If the curve  $y = Ax^n$  revolves about the axis of x, forming a solid, to determine the positions of the nodes when a laterally vibrating free-free bar is formed from two equal halves fitted together at their thicker ends, each



half being a section of the solid by the plane x = l. The bar is of length 2l, and is shown in the figure. If the circular ring of centre P lies in a nodal plane, it is at once evident that the ratio OP/l is a function only of the index n. By the detailed discussion of suitable cases, it is possible to derive an interpolation formula giving the ratio OP/l as a function of n, from which the position of P in any practical case can be found. The results are independent of the absolute dimensions of the bar, and the range of variation of n is between zero and unity.

Attention will be confined to the fundamental bi-nodal vibration, in which the two nodes are equidistant from the free ends. The ratio OP/2l will be called the "nodal ratio," and, in the case of a uniform bar, its value is known to be 0.2242. Apart from Lord Rayleigh's discussion of the effect of a slight lack of uniformity in the cross-section,† which is not applicable to problems of the type now contemplated, the only detailed treatment of a bar of non-uniform section appears to be that of Kirchhoff,‡ who has discussed the vibrations in two cases which admit of a fairly simple solution in terms of Bessel functions. One relates to a rod of prismatic section, and the other to a sharp cone, which is relevant to our present object, being a special case of the solid generated by the revolution of the curve  $y = Ax^n$ , with n = 1, round its axis. Kirchhoff, however, has not treated the double cone or discussed the positions of nodal planes.

When rotatory inertia is neglected—in accordance with the well-known discussion of its effect and degree of importance given by Lord Rayleigh§—and when the displacements are retained only to the first order after the usual manner of small oscillations, the equation of motion may be obtained very simply in the usual form,

$$\partial^{2}\mathbf{M}/\partial x^{2} + \omega \rho$$
 .  $\partial^{2}y/\partial t^{2} = 0$ ,

<sup>\*</sup> Lord Rayleigh, 'Theory of Sound,' vol. 1, p. 256.

<sup>†</sup> Loc. cit., p. 264.

<sup>1 &#</sup>x27;Sitz. der Akad. zu Berlin,' 1879, p. 815.

<sup>§</sup> Loc. cit., p. 289.

where  $\rho$  is the density of the material,  $\omega$  its cross-section at distance x from the origin, taken for convenience at a free end, and M the bending moment, given by

 $\mathbf{M} = \mathbf{E} \boldsymbol{\omega} \kappa^2 \partial^2 y / \partial x^2.$ 

The displacement at any point x is y, E is the modulus of elasticity, and  $\kappa$  the radius of gyration of the area of cross-section about an axis in its plane through its centroid and perpendicular to that of the bar. We only consider circular sections, for which  $\kappa^2 = \frac{1}{4}r^2$ , where r is the radius at the point x, or

$$r = Ax^n$$

Thus

$$\omega = \pi r^2 = \pi A^2 x^{2n}, \qquad \kappa^2 = \frac{1}{4} r^2 = \frac{1}{4} A^2 x^{2n},$$

and the equation of motion becomes

$$\frac{\partial^2}{\partial x^2} \left( \frac{1}{4} \pi \mathbf{E} \mathbf{A}^2 x^{4n} \frac{\partial^2 y}{\partial x^2} \right) + \pi \rho \mathbf{A}^2 x^{2n} \frac{\partial^2 y}{\partial t^2} = 0.$$

For a vibration of period  $2\pi/p$ ,

$$\partial^2 y/\partial t^2 = -p^2 y,$$

and therefore

$$\frac{\partial^2}{\partial x^2} \left( x^{4n} \frac{\partial^2 y}{\partial x^2} \right) = \alpha x^{2n} y,$$

where

$$\alpha = 4\rho p^2/EA^2.$$

If z = qx,  $q^{2n-4} = EA^2/4\rho p^2$  (say),

where z is a new variable, we find

$$\frac{\partial^2}{\partial z^2} \left( z^{4n} \frac{\partial^2 y}{\partial z^2} \right) = z^{2n} y, \tag{2}$$

(1)

as the characteristic differential equation. It is convenient to discuss the special case of a double conical rod before proceeding to its general treatment.

The Conical Rod.—In this case, n=1, and it is possible to write the differential equation in the form

$$\left(\frac{1}{z^2}\frac{\partial}{\partial z}z^3\frac{\partial}{\partial z}\right)^2 y = y,$$

so that solutions of the equations

$$\frac{1}{z^3} \frac{\partial}{\partial z} z^3 \frac{\partial y}{\partial z} = \pm y \tag{3}$$

are solutions of the equation of the fourth order. This reduction to two equations of the second order is not, however, possible for any value of n. The new equations become

$$z\partial^2 y/\partial z^2 + 3\partial y/\partial z = \pm y.$$

When the lower sign is taken in the ambiguity, the general solution becomes

$$y = z^{-1} \{ AJ_3(2\sqrt{z}) + BY_3(2\sqrt{z}) \},$$

where J<sub>2</sub> is the Bessel function of order 2, and Y<sub>2</sub> the corresponding logarithmic function. With the upper sign of the ambiguity,

$$y = z^{-1} \{ CI_2(2\sqrt{z}) + DK_2(2\sqrt{z}) \},$$

the functions being now the so-called "Bessel functions of imaginary argument," and K<sub>2</sub> being logarithmic. The general solution of the fundamental equation is

$$y = z^{-1} \{ AJ_2(2\sqrt{z}) + BY_2(2\sqrt{z}) + CI_2(2\sqrt{z}) + DK_2(2\sqrt{z}) \},$$
 (4)

where A, B, C, D are constants determined by the conditions of support of the bar.

If the end z=0 is free, B=D=0, so that the displacement may not be infinite like  $\log x$ . The shearing stress and bending moment are respectively proportional to

$$z^4 \frac{\partial^2 y}{\partial z^2}, \qquad \frac{\partial}{\partial z} \left( z^4 \frac{\partial^2 y}{\partial z^2} \right),$$
 (5)

and vanish with z under the same circumstances. Thus when z = 0 is a free end

$$y = z^{-1} \{ AJ_2(2\sqrt{z}) + CI_2(2\sqrt{z}) \}.$$
 (6)

As stated already, we only consider, in detail, the bar made up of two precisely equal ends. If its length is 2l, the other end is x = 2l, or

$$z = x(4\rho p^2/\mathrm{EA}^2)^{\delta} = 2l(4\rho p^2/\mathrm{EA}^2)^{\delta} = 2\beta \quad \text{(say)}. \tag{7}$$

When the bar is vibrating symmetrically in the bi-nodal vibration, the displacements at the points x and 2l-x, or z and  $2\beta-z$ , are equal. Thus, for the bar between x=l and x=2l,

$$y(2\beta - z) = AJ_2\{2\sqrt{(2\beta - z)}\} + CI_2\{2\sqrt{(2\beta - z)}\},$$
 (8)

the centre of the bar corresponding to  $z = \beta$ .

The displacement y and its derivative, as given by (6) and (8), must be continuous at x = l or  $z = \beta$ . Moreover, by symmetry,  $\partial y/\partial z = 0$ , and the shearing stress is zero, at the same position. These conditions are not independent.

When  $z = \beta$ , y is evidently continuous from (6) and (8). Since

$$\frac{d}{dz} \cdot z^{-1} J_2(2\sqrt{z}) = -z^{-3/2} J_3(2\sqrt{z}), \quad \frac{d}{dz} \cdot I_2(2\sqrt{z}) = z^{-3/2} I_3(2\sqrt{z}),$$

the condition dy/dz = 0 at  $z = \beta$  yields

$$AJ_3(2\sqrt{\beta}) - CI_3(2\sqrt{\beta}) = 0.$$
 (9)

The same condition follows from the continuity of dy/dz, for its values are

equal and opposite on either side of  $z = \beta$ , and therefore zero;  $d^2y/dz^2$  is continuous at  $z = \beta$  automatically by (6) and (8), since

$$\frac{d^2}{dz^2}z^{-1}J_2(2\sqrt{z}) = z^{-2}J_4(2\sqrt{z}), \quad \frac{d^2}{dz^2}z^{-1}I_2(2\sqrt{z}) = z^{-2}I_4(2\sqrt{z}).$$

The final condition is that obtained from the absence of shearing stress at  $z = \beta$ , or

$$\frac{\partial}{\partial z} \cdot z^4 \frac{\partial^2 y}{\partial z^2} = 0,$$

which becomes

$$\frac{d}{dz} \cdot z^{2} \left\{ AJ_{4}(2\sqrt{z}) + CI_{4}(2\sqrt{z}) \right\} = 0,$$

$$AJ_{3}(2\sqrt{\beta}) + CI_{3}(2\sqrt{\beta}) = 0.$$
(10)

or

Comparing (9) and (10), it is evident that C = 0, and that the period equation is

$$J_8(2\sqrt{\beta}) = 0. \tag{11}$$

The functions of Type I thus disappear for a double conical bar vibrating symmetrically, and the period equation is simpler than in any of the cases treated by Kirchhoff.

The displacement becomes

$$y = Az^{-1}J_2(2\sqrt{z})$$

and the nodes occur where

$$J_2(2\sqrt{z}) = 0. (12)$$

With

$$z = qx = x(4\rho p^2/EA^2)^{\frac{1}{2}}$$
 as in (1)

the nodes are at

$$J_2\{2\sqrt{(qx)}\}=0$$
, where  $J_3\{2\sqrt{(ql)}\}=0$ ,

the length of the rod being 2l.

For the fundamental vibration, quoting the known values of the roots of these equations,\*

$$2\sqrt{(ql)} = 6.379, \qquad 2\sqrt{(qx)} = 5.135,$$
 (13)

and the nodal ratio is x/2l = 0.3240.

In the second tone,

$$2\sqrt{(ql)} = 9.760,$$
  
 $2\sqrt{(qx)} = 5.135, 8.417,$  (14)

the ensuing nodal ratios being 0.1384, 0.3769.

For the third,

$$2\sqrt{(ql)} = 13.017,$$
  
 $2\sqrt{(qx)} = 5.135, 8.417, 11.620,$  (15)

and the three nodal ratios are 0.0778, 0.20905, 0.3984.

<sup>\*</sup> Bourget, 'Ann. de l'École Normale,' vol. 3 (1866).

The three gravest notes emitted in the symmetrical vibrations are, since in the formula for q, A = d/l, where d is the radius of the thickest cross-section,

$$p^2 = \frac{Ed^2q^2}{4\rho l^2} = \frac{Ed^2}{64\rho l^4} (6.379, 9.760, 13.017)^4$$

and their periods are

$$\frac{2\pi}{p} = 16\pi \frac{l^2}{d} \cdot \sqrt{\frac{\rho}{E}} \cdot (6.379, 9.760, 13.017)^{-2}. \tag{16}$$

The General Period Equation.—Whatever the value of n in (2) within certain limits, it usually occurs that the equation has two solutions inapplicable, on account of an infinity, to a free end at x=0. For a free-free bar consisting of two similar halves, the appropriate solution is therefore of the form

$$y = \mathbf{A}\phi(x) + \mathbf{B}\psi(x),\tag{17}$$

where A and B are two arbitrary constants. In the case of symmetrical vibrations,  $\partial y/\partial z = 0$  and

$$\frac{\partial}{\partial z} \cdot z^{4n} \frac{\partial^2 y}{\partial z^2} = 0$$

at the centre. Thus

$$\mathbf{A}\phi'(z) + \mathbf{B}\psi'(z) = 0,$$

$$A \frac{d}{dz} \cdot z^{4n} \frac{d^2 \phi}{dz^2} + B \frac{d}{dz} \cdot z^{4n} \frac{d^2 \psi}{dz^2} = 0,$$

when  $z = \beta$ , the central value. Eliminating A and B, the period equation becomes, if  $P = \phi(z)$ ,  $Q = \psi(z)$ ,

$$P'\frac{d}{dz} \cdot z^{An}Q'' - Q'\frac{d}{dz} \cdot z^{An}P'' = 0, \tag{18}$$

the accent denoting differentiation to z, with  $z = \beta$ .

When P and Q are expressed in series, it is necessary to express the left side of this equation also as a series, and its general term can always be found by use of a differential equation, of higher order, which we may call a "differential period equation." This will now be obtained.

If in (2) we write  $z = e^{\theta}$ ,  $D \equiv d/d\theta$ , it becomes, in terms of this new variable  $\theta$  or  $\log z$ ,

$$D(D-1)(D+4n-2)(D+4n-3)y = ye^{(4-2n)\theta}.$$
 (19)

Let P and Q be any two solutions. Then

$$P \frac{d}{dz} \cdot z^{4n} Q'' - Q \frac{d}{dz} \cdot z^{4n} P''$$

$$= \{ PD(D-1)(D+4n-2)Q - QD(D-1)(D+4n-2)P \} e^{(4n-3)\theta}. \quad (20)$$

Let the bracket be called u. Then the period equation is

$$\frac{d}{d\theta}(ue^{(4n-3)\theta}) = 0, (21)$$

where  $e^{\theta} = \beta$ . We form a differential equation for u.

Let  $P_rQ_s$  be a symbolic representation of  $D^rP$ .  $D^sQ - D^rQ$ .  $D^sP$ , so that  $P_rQ_r = 0$ , and, for example,  $D(P_rQ_{r+1}) = P_rQ_{r+2} + P_{r+1}Q_{r+1} = P_rQ_{r+2}$ . Moreover,  $P_rQ_s = -P_sQ_r$ , and

$$u = PQ_3 + (4n - 3) PQ_2 - (4n - 2) PQ_1,$$
 (22)

and we have by (19),

$$-QP_4 = PQ_4$$

$$= PQe^{(4-2n)\theta} - (8n-6)PQ_3 - (16n^2 - 28n + 11)PQ_2 + (4n-2)(4n-3)PQ_1$$
  
= -(8n-6)PQ\_3 - (16n^2 - 28n + 11)PQ\_2 + (4n-2)(4n-3)PQ\_1,

$$-Q_2P_4 = P_2Q_4 = P_2Q_4 = P_2Q_4 = (4n-3)P_2Q_3 + (4n-2)(4n-3)P_2Q_1$$

and so on. These examples illustrate the main properties of the symbolic notation. We find

$$Du + (4n-3)u = P_1Q_2 + (4n-3)P_1Q_2.$$
 (23)

$$(D+4n-3)^2 u = (4n-2) P_1 Q_2 + P_2 Q_3 + P_1 Q_4 e^{(4-2n)\theta}, \qquad (24)$$

whence, by differentiation,

1) 
$$(D+4n-3)^2u = \{2P_2Q + (4-2n)P_1Q\}e^{(4-2n)\theta} - (8n-6)P_2Q_8 + (4n-2)P_1Q_8 - (4n-2)(4n-3)P_1Q_8.$$
 (25)

and, combining the last three equations,

$$2P_2Q + (6n - 2)P_1Q = \psi, \tag{26}$$

where  $\psi = e^{(3n-4)\theta} (D+4n-3)(D+4n-4)(D+8n-5) u.$  (27)

By further differentiation,

$$D\psi = 2P_2Q + 2P_2Q_1 + (6n - 2)P_2Q_1$$

or, eliminating PaQ and PaQ by (22) and (26),

$$4u + (2D + 2n - 4)\psi = 4P_2Q_1 + 6n(2n - 2)P_1Q.$$
 (28)

Again differentiating, and eliminating P<sub>2</sub>Q<sub>1</sub> (or P<sub>1</sub>Q<sub>3</sub>) and P<sub>2</sub>Q,

$$8(2D+4n-3)u+\{4D^2+(4n-8)D-6n(2n-2)\}$$

$$= -8(4n-3)P_2Q_1 - 6n(2n-2)(6n-2)P_1Q, (29)$$

and performing the same operations again,

$$8 \{D^{3} + (n-2)D^{2} - 3n(n-1)D + 3n(n-1)(3n-1)\} \psi$$

$$+ 16 \{2D^{2} + (4n-3)D - (4n-3)(D + 4n-3)\} u$$

$$= 16 (4n-3)^{2} P_{3}Q_{1} + 48n(n-1)(3n-1)^{3} P_{1}Q. \quad (30)$$

Finally eliminating P<sub>2</sub>Q<sub>1</sub> and P<sub>1</sub>Q from (28-30), and rearranging terms,

$$(D+6n-6)(D+6n-7)(D+2n-5)(D+4n-3)(D+4n-4)(D+8n-5)u$$

$$= -2e^{(4-2n)\theta}(D+4n-3)(2D+6n-2)u. \quad (31)$$

which is the required differential equation of the sixth order, from which the period equation may be derived. Its use is not, in fact, restricted to the special forms of end-conditions with which this paper deals, and its order can be reduced in many cases.

The Double Paraboloid.—We proceed to a detailed calculation for a freefree rod composed of two equal halves, as in the case of the double conical rod, each half being bounded, in any plane through the axis, by the parabola

$$y = Ax^{\frac{1}{2}}$$

between x = 0 and x = 1. Thus  $n = \frac{1}{2}$ , and the fundamental equation (19) becomes, since D = zd/dz,

$$(z\partial/\partial z)^{2}(z\partial/\partial z-1)^{2}y=z^{3}y. \tag{32}$$

The two series solutions finite at z = 0 are obtained at once in the forms

$$P(z) = 1 + \frac{z^3}{2^2 3^2} + \frac{z^6}{2^2 3^2 5^2 6^2} + \frac{z^6}{2^2 3^2 5^2 6^2 8^2 9^2} + \dots$$

$$Q(z) = z + \frac{z^4}{3^2 4^2} + \frac{z^7}{3^2 4^2 6^2 7^2} + \frac{z^{10}}{3^2 4^2 6^2 7^2 9^2 10^2} + \dots$$
(33)

Thus

$$u = P \cdot D^{2}(D-1)Q - QD^{2} \cdot D - 1 \cdot P$$
,  $D \equiv zd/dz$  by (20),

begins with a term in  $z^4$ . The equation (31) of the sixth degree becomes  $(D-1)^2(D-2)(D-3)(D-4)^2u = -2z^2(D-1)(2D+1)u$ , D = zd/dz, and its series solution, with the leading term  $z^4$ , is

$$u = z^{4} - \frac{2z^{7} \cdot 9}{3 \cdot 4 \cdot 5 \cdot 6^{2}} + \frac{2^{2}z^{10} \cdot 9 \cdot 15}{3 \cdot 4 \cdot 5 \cdot 6^{2} \cdot 6 \cdot 7 \cdot 8 \cdot 9^{2}} - \frac{2^{8}z^{13} \cdot 9 \cdot 15 \cdot 21}{3 \cdot 4 \cdot 5 \cdot 6^{2} \cdot 6 \cdot 7 \cdot 8 \cdot 9^{2} \cdot 9 \cdot 10 \cdot 11 \cdot 12^{2}} + \dots$$
(34)

The period equation is, by (21),

$$\frac{d}{dz}\left(\frac{u}{z}\right) = 0, \qquad (z = \beta),$$

which takes the form

$$\sigma - \frac{2\sigma^{3} \cdot 4!}{5!(2!)^{3}} + \frac{3\sigma^{3} \cdot 6!}{8!(3!)^{3}} - \frac{4\sigma^{4} \cdot 8!}{11!(4!)^{3}} + \dots = 0$$
 (35)

when

This series is very convergent, as are the corresponding series for other of

the more interesting values of n. The first solution of the equation is readily found to be

$$\sigma = 22.430, \quad \beta = (3\sigma)^{\frac{1}{2}} = 4.0674, \quad (36)$$

whence

$$P' = 3\sigma^{9} \left\{ \frac{1}{2^{9} \cdot 3^{2}} + \frac{2\sigma^{3}}{2^{2} \cdot 3^{3} \cdot 5^{2} \cdot 6^{2}} + \dots \right\} = 1.5889,$$

$$Q' = 1 + \frac{\sigma^{3}}{3^{2} \cdot 4} + \frac{\sigma^{6}}{3^{2} \cdot 4^{2} \cdot 6^{2} \cdot 7} + \dots = 2.9954,$$
(37)

these series being also very convergent, and suitable for calculation, and the displacement is given by the form

$$y = A \left\{ \frac{P(z)}{1.5889} - \frac{Q(z)}{2.9954} \right\}, \tag{38}$$

making y' vanish when  $z = \beta$ . The node occurs where

$$P(z)/Q(z) = 0.5304$$

whose solution is

$$z = 2.374$$
.

Thus for the fundamental vibration,

$$qx = 2.374, ql = 4.067$$
  
and the nodal ratio is  $x/2l = 0.292.$  (39)  
Now by (1)  $q^{4-2n} = 4\rho p^2/EA^2$ ,

and if d is the semi-breadth at the thickest part,  $d = Al^{\dagger}$  defines A, and  $n=\frac{1}{2}$ , so that

$$q^3 = 4\rho p^3 l / Ed^3 = (4.067)^3 / l^3$$

whence the period of the vibration is

$$2\pi/p = 4\pi l^2/d \cdot \sqrt{(\rho/E)} \cdot (4.067)^{-8/2}. \tag{40}$$

The Case n = 3/4.—If n = 3/4, the characteristic equation (19) becomes  $D^{2}(D-1)(D+1)y = z^{5/2}y,$  $D \equiv zd/dz$ 

which admits two solutions finite at z = 0, in the forms

$$P(z) = 1 + \frac{16z^{5/2}}{3 \cdot 5^{3} \cdot 7} + \frac{16^{3} \cdot x^{10/2}}{3 \cdot 5^{2} \cdot 7 \cdot 8 \cdot 10^{2} \cdot 12} + \frac{16^{3}x^{15/2}}{3 \cdot 5^{2} \cdot 7 \cdot 8 \cdot 10^{2} \cdot 12 \cdot 13 \cdot 15^{3} \cdot 17} + \dots,$$

$$Q(z) = z^{2/2} + \frac{16z^{7/2}}{5 \cdot 7^{2} \cdot 9} + \frac{16^{3} \cdot z^{12/2}}{5 \cdot 7^{3} \cdot 9 \cdot 10 \cdot 12^{3} \cdot 14} + \dots$$

$$(41)$$

The function

$$u = PD(D-1)(D+1)Q-QD(D-1)(D+1)P$$

has a leading term  $z^{7/2}$ , and satisfies the equation of the sixth order

$$(D-\frac{5}{4})(D-\frac{7}{4})(D-\frac{7}{4})D(D-1)(D+1)u = 2x^{5/2}D(2D+\frac{5}{4})u, \quad (42)$$

whose series solution with this leading term is, in powers of  $z^{\dagger}$ ,

$$u = \sum_{\nu}^{\infty} a_{\nu} z^{n/2}.$$

where

$$(n-2)(n+2)(n+3)(n+5)(n+7)a_{n+5} = -32(2n+5)a_n$$

so that

$$u = z^{7/3} - \frac{32z^{13/2} \cdot 19}{5 \cdot 9 \cdot 10 \cdot 12 \cdot 14} + \frac{32^3z^{17/2} \cdot 19 \cdot 29}{5 \cdot 9 \cdot 10 \cdot 12 \cdot 14 \cdot 15 \cdot 17 \cdot 19 \cdot 20 \cdot 22 \cdot 24} - \dots$$
(43)

The period equation is

$$\left[\frac{d}{dz}\cdot uz^{4n-3}\right]_{z=\beta}=0,$$

or finally

$$0 = 7 - \frac{\sigma.12.19}{5.9.10.12.14} + \frac{\sigma^{2}.17.19.29}{5.9.10.12.14.15.17.19} - \frac{\sigma^{3}.22.19.29.39}{5.9.10.12.14.15.17.19.20.22.24} + \dots, (44)$$

where

whence

$$\sigma = 32\beta^{5/2}.$$

The first root can be determined to four significant figures by including only five terms of the series. If  $\sigma = 12600\tau$ , we find

$$7 - 38\tau + 29\tau^2 - 7917\tau^3/1292 + 361179\tau^4/1136960 = 0,$$
  
$$\tau = 0.21966, \quad \sigma = 2767.7, \quad \beta = 5.9537 = gl. \tag{45}$$

The period of the bar is then determined. The shape of one-half is given by the equation  $y = Ax^{3/4}$ , whence, if d is the half-breadth at its centre,

$$A^{4} = d^{4}/l^{3}, \text{ and}$$

$$q = (4\rho p^{2}/EA^{2})^{1/(2n-4)}, \qquad n = \frac{3}{4},$$

$$q^{5} = (16\rho^{2}p^{4}/E^{2}A^{4}) = (5.9519)^{5}/l^{5},$$

$$= 16p^{4}\rho^{2}l^{3}/E^{2}d^{4},$$

$$(5.9510)^{-5}l^{4}$$

so that

$$2\pi/p = 4\pi\sqrt{(\rho/E)} \cdot l^2/d \cdot (5.9519)^{-5/4}. \tag{46}$$

The general formula is in fact

$$2\pi/p = 4\pi\sqrt{(\rho/E)} \cdot l^2/d \cdot (ql)^{n-2}$$
 (47)

for any value of n.

For the values of P and Q in (41),

$$P'(5.9519) = 1.4394, \quad Q'(5.9519) = 3.4612,$$

and the nodes occur where

$$P(z)/1.4394 = Q(z)/3.4612,$$
 (48)

whose solution is z = 3.693, so that the nodal ratio is z/2l, becoming 0.3101. The values of this ratio for  $n = \frac{1}{4}$  and n = 1 were 0.292, 0.324, and the value for  $n = \frac{3}{4}$  is almost precisely the mean of these, so that the change with n is practically uniform in this region. This uniformity, however, does not extend to n = 0, in which case the ratio is 0.2242, and in order to obtain material for subsequent interpolation a separate investigation for  $n = \frac{1}{4}$  is desirable.

The Case  $n = \frac{1}{4}$ .—For this value of n, the characteristic equation becomes  $D(D-1)^{2}(D-2)y = y \cdot z^{1/2}, \qquad D = z\partial/\partial z.$ 

and gives three series solutions, whose leading terms are 1, z,  $z^2$ . The fourth solution is of a logarithmic type which cannot occur with a free end at z=0. The bending moment at the free end is proportional to  $z\,d^2y/dz^2$  and vanishes for the form

$$y = A(1 + \alpha z^{7/2} + ...) + B(z + \beta z^{9/2} + ...) + C(z^2 + \gamma z^{11/2} + ...)$$

derived from these three solutions. The shearing stress, which is the derivate of the bending moment, will not vanish unless C = 0. Thus only two of the series solutions, P and Q, are required, where we find

$$P = 1 + \frac{16x^{7/2}}{3 \cdot 5^2 \cdot 7} + \frac{16^2x^{14/2}}{3 \cdot 5^2 \cdot 7 \cdot 10 \cdot 12^2 \cdot 14} + \dots,$$

$$Q = x^{2/2} + \frac{16x^{9/2}}{5 \cdot 7^2 \cdot 9} + \frac{16^3x^{16/2}}{5 \cdot 7^2 \cdot 9 \cdot 12 \cdot 14^2 \cdot 16} + \dots$$
(49)

Moreover

$$u = x^{9/2} - \frac{17 \cdot 32x^{16/2}}{7^2 \cdot 10^2 \cdot 12} + \frac{17 \cdot 31 \cdot 32^2x^{23/2}}{7^2 \cdot 10^2 \cdot 12 \cdot 14^3 \cdot 17^2 \cdot 19} + \frac{17 \cdot 31 \cdot 45 \cdot 32^3x^{20/2}}{7^2 \cdot 10^2 \cdot 12 \cdot 14^3 \cdot 17^2 \cdot 19 \cdot 21^2 \cdot 24^2 \cdot 26} + \dots, (50)$$

and the period equation is

$$\left[\frac{d}{dz}\cdot uz^{-2}\right]_{z=\beta}=0,$$

whose first solution is found to be

$$\beta = ql = 3.0296, \quad P'(\beta) = 1.8393, \quad Q'(\beta) = 2.6387$$
 (51)

after calculation. The node is given by

$$Q(z)/P(z) = 2.6387/1.8393 = 1.4346,$$
 (52)

whence, by trial and error, z = 1.603 = qx. The nodal ratio is

$$x/2l = 0.2646, (53)$$

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and the fundamental vibration has a period

$$2\pi/p = 4\pi\sqrt{(\rho/E)} \cdot l^2/d \cdot (3.0296)^{-7/4}$$
 (54)

with the usual significance of d.

Discussion of the Results.—In the following Table, the main results worked out in detail are summarised, for the fundamental symmetrical vibration corresponding to any value of n in the equation of the boundary. Those for n = 0 are already well known. The length of the rod is 2l, and the greatest breadth 2b.

n.	Nodal ratio.	Frequency $\times \frac{d}{4\pi l^2} \sqrt{\frac{E}{\rho}}$	
0 .	0.2242	$(4.7800)^{2/4} = 5.598$	
0.25	0 .2646	$(8.0296)^{7/4} = 6.957$	
0.5	0.2920	$(4.0674)^{3/2} = 8.203$	
0.75	0.3101	$(5.9531)^{6/4} = 9.800$	
1.0	0.3240	$(3.1895)^2 = 10.173$	

The frequency rises with the value of n, but not in a linear manner, and an interpolation formula in powers of n between 0 and 1 is not satisfactory, though it can be used over a range of extent only 0.5. The nodes move towards the centre, as would be expected, as n increases, although the nodal ratio is not quite suitable for the usual mode of interpolation except over more limited ranges. But when a great degree of accuracy is not required the interpolation formula

Ratio = 
$$0.074 + 0.3 [(4n+1)/(4n+2)]$$
 (55)

gives good results. It may be illustrated by the spicules mentioned in the introduction, which, on the magnified drawings described in the other paper, had a length whose mean value was about 80 mm. The actual values given by the interpolation formula are:

$$n = 0$$
 0.25 0.5 0.75 1.0  
Ratio = 0.224 0.274 0.299 0.314 0.324  
 $\Delta = 0.0$  + 0.009 + 0.007 + 0.004 0.0

where  $\Delta$  is the error. The greatest error in nodal length on any spicule between n=0.5 and n=1.0, to which region the values of n were always found to be restricted, cannot exceed  $0.007 \times 80$  mm., or 0.54 mm., which is within the possible error of measurement. The use of this formula in the paper is therefore justified.

It is evident that the most important determining feature in the nodal distance is the mean value of  $\omega \kappa^3$  along the rod, and the factor (4n+1)/(4n+2) is contained in the mean, so that the type of formula has some physical basis. The best formula which can apparently be found is

Ratio = 
$$0.2155 - 0.1518[(4n+1)/(4n+2)] + 0.3384[(4n+1)/(4n+2)]^2$$
(56)

with three constants, giving the values

$$n = 0$$
 0.25 0.5 0.75 1.00  
Ratio = 0.2242 0.2647 0.2920 0.3106 0.3240  
 $\Delta = 0.0$  + 0.0001 + 0.0 + 0.0005 0.0

and the ratios for any values of n between 0 and 1 are now known with great precision.

A formula which will give the frequencies with great accuracy is

Frequency = 
$$\frac{d}{4\pi l^2} \sqrt{\frac{E}{\rho}}$$
.  $m$ ,

where 
$$m = 16.237 - 0.400n(n-1)(2n-1) - 10,644(0.8688)^{4n}$$
. (57)

The errors in the values of m thus obtained are 0.0, -0.002, 0.0, -0.003, 0.0 respectively, corresponding to the entries for n in the Table. The extent to which these interpolation formulæ can be used outside the range n=0 to 1 has not been investigated. In the last formula, l and d are the semilength and semi-greatest breadth of the bar.

General Considerations.—For the purpose of numerical computation, solutions, such as that given for n=1, in terms of Bessel functions are not of greater advantage. If the case n=1 were treated by the present method, we should find

$$P(z) = 1 + \frac{z^{2}}{1 \cdot 2 \cdot 3 \cdot 4} + \frac{z^{4}}{1 \cdot 2 \cdot 3^{2} \cdot 4^{2} \cdot 5 \cdot 6} + \dots,$$

$$Q(z) = z + \frac{z^{3}}{2 \cdot 3 \cdot 4 \cdot 5} + \frac{z^{5}}{2 \cdot 3 \cdot 4^{2} \cdot 5^{2} \cdot 6 \cdot 7} + \dots = 0,$$
(58)

and the period equation

$$2 - \frac{3 \cdot 4\beta^2}{2 \cdot 5 \cdot 6 \cdot 8} + \frac{4 \cdot 4^2 \beta^4}{2 \cdot 5 \cdot 6 \cdot 8 \cdot 4 \cdot 7 \cdot 8 \cdot 10} + \dots = 0, \tag{59}$$

whose first solution is easily verified to be  $\beta = 10^{\circ}17$ , in agreement with the first root of  $J_3(2\sqrt{\beta}) = 0$ , which is an equation in powers of  $\beta$  and not of  $\beta^2$ . The period equation in fact contains  $J_3(2\sqrt{\beta})$  as a factor, and the other factor is not oscillatory.

Kirchhoff's investigation of the conical rod appears to imply that it is the only form derived from a revolution of the curve  $y \propto x^n$ , which admits a solution in terms of Bessel functions. This is not in fact the case, for some other forms possess this property. Their complete classification would lead us too far from the special problem investigated in this paper, but the following may be cited as examples:—

(a)  $n = \frac{1}{2}$ .—The complete solution of the equation

$$\frac{d^2}{dz^2} \cdot z^{16/5} \frac{d^2 y}{dz^2} = z^{8/5} y$$

$$y = z^{1/2} \{ AJ_{5/6} (\frac{5}{8} z^{3/5}) + BJ_{-5/6} (\frac{5}{8} z^{3/5}) + CI_{5/6} (\frac{5}{8} z^{3/5}) + DI_{-5/6} (\frac{5}{8} z^{3/5}) \}. \quad (60)$$

(b) n = 3.—The complete solution of the equation

$$\frac{d^2}{dz^2} \cdot z^{12} \, \frac{d^2 y}{dz^2} = z^6 y$$

is  $y = z^{-5} \{ AJ_{10}(2z^{-1/2}) + BY_{10}(2z^{-1/2}) + CI_{10}(2z^{-1/2}) + DK_{10}(2z^{-1/2}) \},$  (61) where Y and K are logarithmic.

## Summary.

The paper contains a discussion of the lateral vibrations of a bar composed of two equal halves, and free at each end. Each half consists of a portion of the solid generated by the revolution of the curve  $y = Ax^n$  about its axis, and the fundamental frequencies and positions of the corresponding nodes are investigated for various values of n between 0 and 1.

The investigation proceeds according to a general method of determining the period equation as a series of ascending powers of a variable whose general term can be found from a differential equation of the sixth order. The special values of n for which computations are made were selected in accordance with the needs of a preceding paper on the vibrations of sponge-spicules by Prof. Dendy and the writer.

The dependence of the frequency and nodal distance on the index n is finally expressed by interpolation formulæ which can give an accuracy of about 1 part in 100, within the range n = 0 to n = 1.

## Some Cases of Wave Motion due to a Submerged Obstacle: By T. H. HAVELOCK, F.R.S.

## (Received May 14, 1917.)

1. As far as I am aware, only one case of wave motion caused by a submerged obstacle has been worked out in any detail, namely the two-dimensional motion due to a circular cylinder; for this case, Prof. Lamb has given a solution applicable when the cylinder is of small radius and is at a considerable depth.\* The method can be extended to bodies of different shape, and my object in this paper is to work out the simplest three-dimensional case, the motion of a submerged sphere.

The problem I have considered specially is the wave resistance of the submerged body. In the two-dimensional case, this is calculated by considerations of energy and work applied to the train of regular waves. But for a moving sphere the wave system is more complicated, like the well-known wave pattern for a moving point disturbance, and similar methods are not so easily applied; I have therefore calculated directly the horizontal resultant of the fluid pressure on the sphere. Before working out this case, the analysis for the circular cylinder is repeated, because it is necessary to carry the approximation a stage further than in Prof. Lamb's solution in order to verify that the resultant horizontal pressure on the cylinder is the same as the wave resistance obtained by the method of energy.

The stages in approximating to the velocity potential may be described in terms of successive images; the first stage  $\phi_1$  is the image of a uniform stream in the submerged body, the second stage  $\phi_2$  is the image of  $\phi_1$  in the free surface, the third  $\phi_3$  is the image of  $\phi_2$  in the submerged body, and so on. In order to keep the integrals convergent, a small frictional coefficient is introduced in the usual manner; after the calculations have been carried out, the coefficient is made zero. Further, the solution for uniform motion is built up so that expressions can be found for the velocity potential at any time after the starting of the motion, although only the final steady state has been studied in detail. The wave resistance of a sphere is found to have the form const.  $\times \alpha^{3/2} e^{-\alpha/2} W_{1,1}(\alpha)$ , in which  $\alpha$  is  $2gf/c^2$ , with f the depth of the sphere and c its velocity;  $W_{1,1}(\alpha)$  is a confluent hypergeometric function. In order to graph the wave resistance as a function of the velocity, expansions have been found for this particular variety of the function

<sup>\*</sup> H. Lamb, 'Ann. di Matematica,' vol. 21, p. 237; also 'Hydrodynamics,' 4th ed., p. 401.

 $W_{k,m}(\alpha)$ ; it belongs to the logarithmic case for which a general expansion is not available.

In general form the graph of the resistance is very similar to that of the circular cylinder.

Circular Cylinder.

2. The steady state for uniform motion of the cylinder may be attacked directly, as in Prof. Lamb's solution, but we shall adopt his suggestion of building it up from simple oscillations. Take the axis of x in the free surface of the water, and the axis of y vertically upwards. A circular cylinder, of radius a, is making small oscillations parallel to 0x with velocity  $c\cos\sigma t$ , the axis of the cylinder being horizontal and perpendicular to 0x, and the mean position of the centre being the point (0, -f). A first appproximation when the depth f is sufficiently large is found by ignoring the surface effect altogether and putting

$$\phi = ca^{2}(x/r^{2})e^{i\sigma t}; \qquad r^{2} = x^{2} + (y+f)^{2}. \tag{1}$$

This satisfies the boundary condition at the surface of the cylinder. For the next step, add a term  $X_1$  to the velocity potential so as to satisfy the conditions at the free surface, but ignoring meantime the disturbance produced thereby at the surface of the cylinder. The term  $X_1$  must be a potential function and it must satisfy the condition for deep water, namely,  $\partial X_1/\partial y = 0$  for  $y = -\infty$ ; these conditions are fulfilled by

$$\mathbf{X}_{1} = e^{i\sigma t} \int_{0}^{\infty} \alpha(\kappa) e^{\kappa y} \sin \kappa x \, d\kappa, \qquad (2)$$

where  $\alpha$  is a function of  $\kappa$  to be determined. This form is chosen because we can satisfy the conditions at the free surface by using an equivalent form for (1), since

$$x/r^2 = \int_0^\infty e^{-\kappa(y+f)} \sin \kappa x \, d\kappa \; ; \qquad y+f > 0. \tag{3}$$

The surface elevation is expressed similarly by

$$\eta = e^{i\sigma t} \int_0^\infty \beta(\kappa) \sin \kappa x \, d\kappa. \tag{4}$$

In order to keep the various integrals convergent, we assume that the liquid has a slight amount of friction proportional to velocity; in the sequel the results are simplified by making the frictional coefficient  $\mu$  tend to zero. In these circumstances the pressure equation is

$$p/\rho = \text{const.} -gy + \mu\phi - \frac{1}{2}q^2. \tag{5}$$

Hence the conditions at the free surface are, neglecting the square of the velocity,

$$-gy + \mu \phi = \text{const.}; \quad -\partial \phi / \partial y = \partial \eta / \partial t.$$

Here  $\phi$  is the velocity potential after (2) has been added to (1); thus the equations for  $\alpha$  and  $\beta$  are

$$c\alpha^{2}\kappa e^{-\kappa f} - \kappa\alpha = i\sigma\beta$$

$$i\sigma c\alpha^{2}e^{-\kappa f} + i\sigma\alpha - g\beta + \mu c\alpha^{2}e^{-\kappa f} + \mu\alpha = 0$$
(6)

From these we obtain the expressions for  $X_1$  and  $\eta$ , namely

$$X_{1} = ca^{2}e^{i\sigma t} \int_{0}^{\infty} \frac{g\kappa + \sigma^{2} - i\mu\sigma}{g\kappa - \sigma^{2} + i\mu\sigma} e^{-\kappa (f-y)} \sin \kappa x \, d\kappa, \tag{7}$$

$$\eta = ca^2 e^{i\sigma t} \int_0^\infty \frac{2\kappa \left(\mu + i\sigma\right)}{g\kappa - \sigma^2 + i\mu\sigma} e^{-\kappa f} \sin \kappa x \, d\kappa. \tag{8}$$

The expression for  $X_1$  can be divided into two parts

$$X_{1} = -ca^{2}e^{i\sigma t} \int_{0}^{\infty} e^{-\kappa(f-y)} \sin \kappa w \, d\kappa - 2ca^{2}e^{i\sigma t} \int_{0}^{\infty} \frac{g\kappa e^{-\kappa(f-y)} \sin \kappa w \, d\kappa}{\sigma^{2} - i\mu\sigma - g\kappa}. \tag{9}$$

If we regard  $X_1$  as the image of the oscillating cylinder in the free surface, we see from the form of the first integral in (9) that part of the image is a negative doublet at the image point (0, f). We obtain next the velocity potential of the motion produced by a sudden small displacement of the cylinder, and we take this to be equivalent to a momentary doublet of constant strength. Suppose then that at a time  $\tau$  a doublet is suddenly created, maintained constant for a time  $\delta \tau$ , and then annihilated. The velocity potential at any subsequent time t is given by a Fourier synthesis of the preceding results for an oscillating cylinder, and we have

$$\phi = \frac{\delta \tau}{\pi} \int_0^\infty e^{i\sigma(t-\tau)} [\phi] d\sigma, \qquad (10)$$

where  $[\phi]$  is the sum of (1) and (9), omitting the factor  $e^{i\sigma t}$ .

Carrying out this integration for the value of  $\phi$  in (1) and for the first part of (9) gives simply the momentary doublet at the centre of the cylinder and the negative doublet at the image point. These doublets last for a short time  $\delta\tau$ ; the subsequent fluid motion is contributed by the second part of (9). For this we have to evaluate the real part of

$$\int_{0}^{\infty} \frac{e^{i\sigma(t-\tau)}}{\sigma^{2} - i\mu\sigma - g\kappa} d\sigma; \qquad t-\tau > 0.$$
(11)

We obtain the value by contour integration; further we simplify the result by neglecting  $\mu^2$ . We shall make  $\mu$  zero ultimately, but we must retain it sufficiently to keep the integrals convergent; however, at one or two stages, superfluous terms may be omitted when it is clear that the final limiting values will not be affected. We find for (11) the value

$$-\pi\kappa\nabla e^{-\frac{1}{2}\mu(t-\tau)}\sin\left\{\kappa\nabla\left(t-\tau\right)\right\},\,$$

writing V for  $\sqrt{(g/\kappa)}$  whenever it serves to simplify the notation. Hence the velocity potential of the subsequent fluid motion after the cylinder has been given a small displacement at time  $\tau$  is

$$\phi = 2ca^2\delta\tau e^{-\frac{1}{4}\mu(t-\tau)}\int_0^\infty \kappa \nabla e^{-\kappa(f-y)}\sin\kappa x\sin\kappa\nabla(t-\tau)d\kappa. \tag{12}$$

Finally we obtain the velocity potential for a cylinder in uniform motion by substituting  $x+c(t-\tau)$  for x, noting that hereafter x will refer to a moving origin immediately over the centre of the cylinder; we then integrate with respect to  $\tau$  from the start of the motion up to the instant in question. We could in this way obtain results for any stage of the motion, but we limit the discussion to the final steady state; for this we take  $-\infty$  as the lower limit in integrating with respect to  $\tau$ . Before writing down the result, we must remember to introduce the integrated effect of the original momentary doublet in (1) and its negative image, which were not included in (11); these clearly add up to steady doublets. Hence we find for the steady state

$$\phi = D - D_1 + 2ca^2 \int_0^\infty e^{-\kappa(f-y)} (A \sin \kappa x + B \cos \kappa x) d\kappa, \qquad (13)$$

where D represents the doublet  $ca^2x/r^2$  at the point (0, -f),  $D_1$  an equal doublet at the point (0, f), and

$$2A = \frac{\kappa^{2}V(V+c)}{\kappa^{2}(V+c)^{2} + \frac{1}{4}\mu^{2}} + \frac{\kappa^{2}V(V-c)}{\kappa^{2}(V-c)^{2} + \frac{1}{4}\mu^{2}},$$

$$4B = \frac{\mu\kappa V}{\kappa^{2}(V-c)^{2} + \frac{1}{4}\mu^{2}} - \frac{\mu\kappa V}{\kappa^{2}(V+c)_{2} + \frac{1}{4}\mu^{2}}.$$
(14)

3. Before proceeding further we may obtain the surface elevation from (13) for comparison. The surface condition is now

$$-\partial \phi/\partial y = \partial \eta/\partial t = -c \,\partial \eta/\partial x.$$

Hence we have

$$\eta = 2a^2 f/(x^2 + f^2) - 2a^2 \kappa_0 \int_0^\infty (A\cos \kappa x - B\sin \kappa x) e^{-\kappa f} d\kappa, \qquad (15)$$

in which  $\kappa_0 = g/c^2$ . Further, since  $\mu$  is to be small, we may omit irrelevant terms and put

$$\mathbf{A} = -\kappa_0 (\kappa - \kappa_0) / \{\kappa - (\kappa_0 + i\mu/c)\} \{\kappa - (\kappa_0 - i\mu/c)\},$$

$$\mathbf{B} = \kappa_0 (\mu/c) / \{\kappa - (\kappa_0 + i\mu/c)\} \{\kappa - (\kappa_0 - i\mu/c)\}.$$
(16)

The integral in (15) can then be written as

$$\int_{0}^{\infty} \left\{ \frac{e^{-i\kappa x}}{\kappa - \kappa_{0} - i\mu/c} + \frac{e^{i\kappa x}}{\kappa - \kappa_{0} + i\mu/c} \right\} e^{-\kappa f} d\kappa. \tag{17}$$

We transform these integrals by contour integration in the plane of a complex variable  $\kappa$ , treating separately the cases of x positive and x negative; after making  $\mu$  zero in the final results we obtain

$$\eta = \frac{2a^2f}{x^2 + f^2} + 4\pi a^2 \kappa_0 e^{-\kappa_0 f} \sin \kappa_0 x + 2a^2 \kappa_0 \int_0^{\infty} \frac{m \cos mf - \kappa_0 \sin mf}{m^2 + \kappa^2} e^{mx} dm \; ; \quad x < 0,$$

$$\eta = \frac{2a^2f}{x^2 + f^2} + 2a^2\kappa_0 \int_0^\infty \frac{m\cos mf - \kappa_0 \sin mf}{m^2 + \kappa^2} e^{-mx} dm \; ; \qquad x > 0.$$
 (18)

These agree with Lamb's results for the circular cylinder in a uniform stream. The wave resistance R is derived from the regular waves in the rear, by considering the rate of increase of energy and taking into account the propagation of energy in a regular train; we have

$$R = \frac{1}{4}g\rho \text{ (amplitude)}^2 = 4\pi^2g\rho\alpha^4\kappa_0^2e^{-2\kappa_0f}. \tag{19}$$

4. We have now to obtain the resistance R by direct summation of the horizontal component of fluid pressure on the cylinder. It is clearly necessary to proceed to a further stage with the velocity potential, since we have assumed so far that the surface effect is negligible in the neighbourhood of the cylinder. If we write (13) as

$$\phi = D + X_1, \tag{20}$$

the doublet D is the first approximation, satisfying the boundary conditions on the cylinder;  $X_1$  is the image of the doublet in the free surface, found by satisfying the conditions there. The next step is to find  $X_2$ , the image of  $X_1$  in the cylinder, ignoring then the effect of  $X_2$  at the free surface. It follows that  $X_2$  is the image of  $X_1$  in the cylinder, found as if the cylinder were at rest in a field defined by  $X_1$ . Taking polar co-ordinates with the origin at the centre of the circular section of the cylinder, we have

$$x = r \cos \theta; \quad y + f = r \sin \theta;$$
 (21)

also the conditions for X<sub>2</sub> are that it should be a potential function, the components of velocity must vanish as r becomes infinite, and

$$\partial (X_1 + X_2)/\partial r = 0$$
, for  $r = a$ . (22)

But from (13), X<sub>1</sub> consists of a summation of terms of the form

$$e^{\kappa y} \frac{\cos}{\sin} \kappa x.$$

We obtain X<sub>2</sub> by replacing each term by the expressions

$$e^{-\kappa f} e^{\kappa a^2 \sin \theta/r} \frac{\cos}{\sin} (\kappa a^2 \cos \theta/r),$$

and the above conditions for  $X_2$  are then satisfied. This process amounts simply to inversion; we may think of  $X_1$  as due to a line distribution of

sources and X<sub>2</sub> is then a circle of sources on the inverse of this line with respect to the cylinder. We have now for the velocity potential to this stage

$$\phi = D + 2ca^{2} \int_{0}^{\infty} e^{-\kappa(f-y)} \{ (A - \frac{1}{2}) \sin \kappa x + B \cos \kappa x \} d\kappa$$

$$+ 2ca^{2} \int_{0}^{\infty} e^{-\kappa f + \kappa a^{2}y/r^{2}} \{ (A - \frac{1}{2}) \sin (\kappa a^{2}x/r^{2}) + B \cos (\kappa a^{2}x/r^{2}) \} d\kappa. \quad (23)$$

We have put  $A - \frac{1}{2}$  for A so as to include under the integral sign the doublet previously denoted by  $D_1$ .

The method could theoretically be carried on step by step; however, we stop at this stage because it is sufficient for obtaining the wave resistance R from the pressure equation to the same approximation as by the energy method.

We have 
$$R = \int_0^{2\pi} \alpha p \cos \theta \, d\theta \,; \qquad (24)$$

$$p/\rho = -c\partial\phi/\partial x - gy + \mu\phi - \frac{1}{2}g^2. \tag{25}$$

If we write (23) as  $\phi = D + X_1 + X_2$ , and omit terms which obviously contribute nothing to the value of R, we have, when r = a,

$$\frac{p}{\rho} = -e\frac{\partial}{\partial x}(X_1 + X_2) + \mu (X_1 + X_2) - \frac{1}{a^2} \frac{\partial D}{\partial \theta} \frac{\partial (X_1 + X_2)}{\partial \theta}$$
$$= (2e/a) \sin \theta \partial (X_1 + X_2)/\partial \theta + \mu (X_1 + X_2), \quad (26)$$

where we have used (22) and the value of D. From (23), omitting the doublets D and  $D_1$ , which will from symmetry give no contribution to R when  $\mu$  is zero, we have

$$p = 4ca^{2} \int_{0}^{\infty} e^{-2\kappa f + \kappa a \sin \theta} \left\{ 2\kappa c A \sin \theta \sin (\phi - \theta) + \mu A \sin \phi + 2\kappa c B \sin \theta \cos (\phi - \theta) + \mu B \cos \phi \right\} d\kappa, \quad (27)$$

where  $\phi = \kappa a \cos \theta$ . Substituting in (24) we have an expression for R. We may now change the order of integration and take first that with respect to  $\theta$ ; we can carry this out, after some transformation, by means of the integrals

$$\int_{0}^{\pi} e^{h\cos\theta} \cos(h\sin\theta - n\theta) d\theta = \pi h^{n}/\Gamma(n+1),$$

$$\int_{0}^{\pi} e^{h\cos\theta} \cos(h\sin\theta + n\theta) d\theta = 0,$$
(28)

where n is a positive, odd integer. In fact the integration with respect to  $\theta$  gives simply  $\pi \kappa a (\kappa c B + \mu A)$ ; hence we have

$$R = 4\pi \rho c a^4 \int_0^\infty \kappa \left(\kappa c B + \mu A\right) e^{-2\kappa f} d\kappa, \qquad (29)$$

where A and B are given by (14), or by (16) since we suppose  $\mu$  small. Thus we have

$$R = 4\pi\rho ca^{4} \lim_{\mu \to 0} \int_{0}^{\infty} \frac{\mu \kappa_{0}^{2} \kappa e^{-2\kappa f} d\kappa}{\{\kappa - (\kappa_{0} + i\mu/c)\} \{\kappa - (\kappa_{0} - i\mu/c)\}}$$

$$= 4\pi\rho ca^{4} \lim_{\mu \to 0} \mu \{2\pi i \kappa_{0}^{3} e^{-2\kappa_{0} f} / 2i (\mu/c) + \text{finite quantity}\}$$

$$= 4\pi^{2} g^{3} \rho a^{4} c^{-4} e^{-2gf/c^{2}}, \tag{30}$$

which is the same as the previous expression (19).

5. A sphere of radius a is at depth f below the surface and is moving with uniform velocity c parallel to the axis of x. The origin is in the free surface, the axis of z being drawn vertically upwards. As before, the first approximation is a doublet D given by

$$\phi = \frac{ca^3x}{2r^3}$$
;  $r^2 = x^3 + y^2 + (z+f)^2$ . (31)

For the purpose of satisfying the conditions at the free surface we have

$$\phi = D = -\frac{1}{2} c a^3 \frac{\partial}{\partial c} \int_0^\infty e^{-\kappa (z+f)} J_0 \{ \kappa \sqrt{(x^2 + y^2)} \} d\kappa ; \qquad z+f > 0. \quad (32)$$

This suggests at once suitable forms for the next approximation and for the free surface; the equations are similar to (6) of the previous case, and we obtain in the same way

$$\phi = D - D_1 + X_1, \tag{33}$$

where  $D_1$  is a doublet at the image point (0, 0, f) and

$$\mathbf{X}_{1} = ca^{3} \frac{\partial}{\partial x} \int_{0}^{\infty} \sqrt{(g\kappa)} e^{-\kappa(f-z)} d\kappa \int_{0}^{\infty} e^{-\frac{1}{2}\mu u} \mathbf{J}_{0} \left[\kappa \sqrt{\{(x+cu)^{2}+y^{2}\}\}} \sin(\kappa \nabla u) du, \right]$$
(34)

The corresponding surface elevation is

$$\eta = \alpha^{3} \int_{0}^{\infty} e^{-\kappa f} J_{0} \{ \kappa \sqrt{(x^{2} + y^{2})} \} \kappa \, d\kappa 
+ \alpha^{3} \int_{0}^{\infty} \sqrt{(g\kappa)} \, e^{-\kappa f} \kappa \, d\kappa \int_{0}^{\infty} e^{-\frac{1}{2}\mu u} J_{0} [\kappa \sqrt{\{(x + cu)^{2} + y^{2}\}}] \sin(\kappa \nabla u) \, du.$$
(35)

The first term represents the effect of the doublets D and D<sub>1</sub>. It can be verified by approximate methods that the second term includes a main part like the well-known wave pattern for ship waves. Since the expression in (35) gives finite and continuous values for the surface elevation, it might be of interest to examine some points in detail; for instance, the elevation near the lines corresponding to the lines of cusps for a moving point disturbance. However, we pass now to the calculation of the resultant horizontal pressure

on the sphere. We have to find  $X_2$  the image of  $X_1$  in the sphere; for this we first put  $X_1$  into a different form by using

$$\pi J_0[\kappa \{(x+cu)^2+y^2\}^{\frac{1}{2}}] = \int_0^\pi \cos\{\kappa (x+cu)\cos\phi\}\cos(\kappa y\sin\phi)\,d\phi. \quad (36)$$

From (36) and (34), after carrying out the integration with respect to u, we obtain

$$\pi \mathbf{X}_{1} = ca^{3} \int_{0}^{\infty} e^{-\kappa(f-x)} \kappa d\kappa \int_{0}^{\pi} \{ \mathbf{A} \sin(\kappa x \cos \phi) + \mathbf{B} \cos(\kappa x \cos \phi) \}$$

$$\times \cos(\kappa u \sin \phi) \cos \phi d\phi. \quad (37)$$

where A and B are given by (14) after writing  $c \cos \phi$  for c.

For convenience in the following analysis, we transfer the origin to the centre of the sphere, noting that in (37) we shall have  $\exp((-2\kappa f + \kappa z))$  in place of  $\exp((-\kappa f + \kappa z))$ . Also we use polar co-ordinates

$$x = r \cos \alpha$$
;  $y = r \sin \alpha \cos \beta$ ;  $z = r \sin \alpha \sin \beta$ .

The conditions for  $X_2$  are that it must be a potential function, the disturbance due to it must ultimately vanish as we recede from the sphere, and on the sphere

$$\partial (\mathbf{X}_1 + \mathbf{X}_2) / \partial r = 0. \tag{38}$$

To avoid repetition of expressions like (37), we take out of it a typical term and write

$$X_1 = e^{\kappa z} \sin(\kappa x \cos\phi) \cos(\kappa y \sin\phi). \tag{39}$$

We know that the function

$$r^{-1}e^{\kappa a^2y/r^2}\sin\left(\kappa a^2x\cos\phi/r^2\right)\cos\left(\kappa a^2y\sin\phi/r^2\right) \tag{40}$$

satisfies the first two conditions for  $X_2$ , but we find it does not fulfil (38). An additional term is required, and it can be found in the following way. Suppose that on the sphere we have

$$e^{\kappa x} \sin(\kappa x \cos \phi) \cos(\kappa y \sin \phi) = \sum A_m Y_m(\alpha, \beta),$$
 (41)

where the right-hand side is an expansion in surface spherical harmonics. Then for the term (39), all the conditions for  $X_2$  are satisfied by

$$ar^{-1}e^{a\alpha^3x/r^2}\sin(\kappa a^2x\cos\phi/r^2)\cos(\kappa\alpha^2y\sin\phi/r^2) - \Sigma a^{m+1}\Lambda_mY_m/(m+1)r^{m+1}.$$
(42)

Suppose, similarly, that on the sphere we have

$$\sigma^{\kappa r}\cos(\kappa x\cos\phi)\cos(\kappa y\sin\phi) = \sum B_m Y_m(\alpha,\beta). \tag{43}$$
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Then the complete expression for X<sub>2</sub> is

$$\pi X_2 = ca^3 \int_0^\infty e^{-2\kappa f} \, \kappa d\kappa \int_0^\pi a r^{-1} e^{\kappa a^2 r/r^2} \cos{(\kappa a^2 y \sin{\phi/r^2})} \cos{\phi}$$

 $\times \{A \sin (\kappa a^2 x \cos \phi/r^2) + B \cos (\kappa a^2 x \cos \phi/r^2)\} d\phi$ 

$$-ca^{3}\int_{0}^{\infty}e^{-2\pi f}\kappa d\kappa\int_{0}^{\pi}\sum_{m}\left(AA_{m}+BB_{m}\right)(m+1)^{-1}(a/r)^{m+1}Y_{m}\cos\phi\,d\phi.$$
(44)

We have now

$$\phi = D - D_1 + X_1 + X_2 = D + X, \tag{45}$$

and the pressure equation is

$$p/\rho = -c \,\partial \phi/\partial x - gz + \mu \phi - \frac{1}{2} \,g^2. \tag{46}$$

The wave resistance, or the resultant horizontal pressure on the sphere, is

$$R = \int_0^{\pi} d\alpha \int_0^{2\pi} \alpha^2 p \sin \alpha \cos \alpha d\beta. \tag{47}$$

Omitting terms which, from symmetry, will give no contribution to R, we have

$$\frac{p}{\rho} = -c\frac{\partial X}{\partial x} + \mu X - \frac{\partial D}{\partial r}\frac{\partial X}{\partial r} - \frac{1}{r^2}\frac{\partial D}{\partial \alpha}\frac{\partial X}{\partial \alpha} - \frac{1}{r^2\sin^2\alpha}\frac{\partial D}{\partial \beta}\frac{\partial X}{\partial \beta}.$$
 (48)

But when r = a, we have

hence

$$\partial D/\partial \beta = 0$$
;  $\partial D/\partial \alpha = -\frac{1}{2}ea\sin \alpha$ ;  $\partial X/\partial r = 0$ ,  $p/\rho = (3c/2a)\sin \alpha \partial X/\partial \alpha + \mu X$ . (49)

We must now substitute (49) in (47) and use the value of X given by the sum of (37) and (44) on the sphere; it is clear that we may omit the doublet  $D_1$  as it will not affect the limiting value of R when  $\mu$  is zero.

6. Consider, in the first place, the contribution of the first term in the value of p given in (49). In the repeated integrals which are obtained, we may change the order of integration, and we shall carry out first the summation over the surface of the sphere. We notice that, when r=a, the first term in the value of  $X_2$  in (44) is equal to the value of  $X_1$ ; the additional part of  $X_2$  is the term involving the expansions in spherical surface harmonics. Choose a typical term from the latter part, and we find we have to evaluate

$$\int_{\frac{\pi}{2}}^{n} \sin \alpha \cos \alpha \left( \frac{\partial Y_m}{\partial \alpha} \right) dS, \tag{50}$$

taken over the surface of unit sphere.

But this integral is equal to

$$-3\left[P_{2}(\cos\alpha)Y_{m}(\alpha,\beta)dS\right] \tag{51}$$

Hence, the only term which has a value different from zero is the term in Y<sub>2</sub>, the surface harmonic of the second order. From the manner in which

the expansions were introduced, in (41) and (43), it follows that the contribution of the second term in (44) is one-third of that of the first term; hence, summing up the result so far as the first term of (49) is concerned, we have

$$\pi R' = -5c^2 a^4 \rho \int_0^\infty e^{-2\kappa f} \kappa d\kappa \int_0^\pi \cos \phi \, d\phi \int_0^{2\pi} d\beta \int_0^\pi \sin \alpha P_2(\cos \alpha) e^{\kappa a \sin \alpha \sin \beta}$$

 $\times \cos(\kappa a \sin \alpha \cos \beta \sin \phi)$ 

$$\times \{A \sin (\kappa a \cos \alpha \cos \phi) + B \cos (\kappa a \cos \alpha \cos \phi)\} d\alpha.$$
 (52)

Taking the integration with respect to  $\beta$ , we find it is equal to

$$2\int_{0}^{\pi} e^{\kappa a \sin \alpha \cos \beta} \cos (\kappa a \sin \alpha \sin \phi \sin \beta) d\beta = 2\pi I_{0} (\kappa a \sin \alpha \cos \phi), \quad (53)$$

where  $I_0(x)$  is the Bessel function  $J_0(ix)$ , a result which may be obtained by direct expansion and integration term by term. For the integration with respect to  $\alpha$  the term in A in (52) obviously gives zero, and we are left with

$$2\pi \int_0^\pi I_0(\kappa a \cos \phi \sin \alpha) \cos (\kappa a \cos \phi \cos \alpha) P_2(\cos \alpha) \sin \alpha d\alpha. \tag{54}$$

Here also we may expand in powers of  $\kappa a$  and integrate term by term; it can be shown that the integral of the coefficient of  $(\kappa a)^n$  vanishes except for the single term  $\kappa^2 a^2$ ; thus we find that (54) reduces to

$$-(2\pi/5)\kappa^2\alpha^2\cos^2\phi$$
.

7. We have now to consider the term  $\mu X$  in the value for p in (49). We might omit this term, on general grounds, as giving no contribution to R ultimately when  $\mu$  vanishes; for X is the velocity potential for a sphere at rest in a given field  $X_1$ . However, it may be left in, and we have a similar calculation. Taking the second integral in (44), we find it is now only the term in  $Y_1$  which counts; hence the contribution of this part is one-half of that of the first integral in (44). Further, it is the term involving A which gives a value different from zero when integrating with respect to  $\alpha$ , and instead of (54) we have

$$2\pi \int_0^{\pi} I_0(\kappa a \cos \phi \sin \alpha) \sin(\kappa a \cos \phi \cos \alpha) P_1(\cos \alpha) \sin \alpha d\alpha$$

which reduces to  $(4\pi/3) \kappa a \cos \phi$ .

8. Collecting the various results, we have now

$$R = -2ca^{6}\rho \int_{0}^{\infty} e^{-2\kappa f} \kappa^{2} d\kappa \int_{0}^{\kappa} (\kappa c \operatorname{B} \cos \phi + \mu A) \cos^{2} \phi d\phi, \qquad (55)$$

a form which may be compared with the corresponding expression for the cylinder in (29).

A and B are given by (14) when we replace c by  $c\cos\phi$ ; putting these values in (55), we see that we may change the order of integration. Further, as we make  $\mu$  vanish ultimately, we may use simplified forms of A and B corresponding to (16). These give

$$\mathrm{R} = 4\kappa_0^2 c a^6 \rho \mu \int_0^{\pi/2} \sec^2\!\phi \, d\phi \int_0^{\infty} \frac{\kappa^2 e^{-2\pi f} \, d\kappa}{(\kappa - \kappa_0 \sec^2\!\phi)^2 + (\mu/e)^2 \sec^2\!\phi} \, .$$

To obtain the limiting value for  $\mu$  zero we may treat this like the similar expressions in (30); or, alternatively, we may put  $(\mu/c) \sec \phi = 1/n$ , and use the general result

$$\lim_{n \to \infty} \int_{a}^{b} \frac{f(x) dx}{1 + n^{2}(x - \alpha)^{2}} = \frac{\pi}{2} \{f(\alpha - 0) + f(\alpha + 0)\}.$$

The apparent difficulty with regard to values of  $\phi$  near  $\pi/2$  is overcome by noticing that with the particular functions involved in R no extra contribution arises from such terms near the upper limits of the variables. Carrying out the integration in  $\kappa$  in this way, and changing the remaining variable by putting  $\tan \phi = t$ , we obtain

$$R = 4\pi g^4 \rho a^6 e^{-6} e^{-2gf/c^4} \int_0^\infty (1 + t^2)^{3/2} e^{-2gft^2/c^2}.$$
 (56)

The remaining integral can be expressed in terms of known functions. Possibly the simplest method is to use the confluent hypergeometric function\* defined, for real positive values of  $\alpha$  and for real values of k and m for which  $k-m-\frac{1}{2} \leq 0$ , by

$$W_{k,m}(\alpha) = \frac{e^{-\alpha/2} \alpha^k}{\Gamma(\frac{1}{2} - k + m)} \int_0^\infty u^{-k - \frac{1}{2} + m} (1 + u/\alpha)^{k - \frac{1}{2} + m} e^{-u} du.$$
 (57)

We have now the wave resistance of the sphere given by

$$R = \frac{1}{4} \pi^{3/2} y \rho \alpha^6 f^{-3} \alpha^{3/2} e^{-\alpha/2} W_{1,1}(\alpha); \qquad \alpha = 2 y f/c^2. \tag{58}$$

8. For purposes of calculation, we require expansions of  $W_{1,1}(\alpha)$ . This function belongs to the logarithmic type of confluent hypergeometric function, and general expansions are not available in this case; however, they can be obtained without difficulty for  $W_{1,1}$ . In the first place, the differential equation satisfied by  $W_{1,1}$  is

$$\frac{d^2y}{d\alpha^2} + \left(-\frac{1}{4} + \frac{1}{\alpha} - \frac{3}{4\alpha^2}\right)y = 0. \tag{59}$$

We use the ordinary methods for solving by means of power series. The roots of the indicial equation are  $\frac{8}{4}$  and  $-\frac{1}{2}$ ; hence one of the fundamental

\* E. T. Whittaker, 'Bull. Amer. Math. Soc.,' vol. 10, p. 125; also Whittaker and Watson, 'Modern Analysis,' Chap. XVI.

solutions will contain logarithms. Calculating the coefficients step by step, we obtain as a fundamental system

$$y_{1} = \alpha^{3/2} \left( 1 - \frac{1}{5} \alpha + \frac{7}{9^{1} 6} \alpha^{2} - \frac{1}{9^{1} 6} \alpha^{3} + \frac{1}{9^{1} 2} \frac{1}{6} \alpha^{4} - \dots \right)$$

$$y_{2} = y_{1} \log \alpha + \alpha^{-3/2} \left( -\frac{5}{5} - \frac{5}{5} \alpha + \frac{2}{3} \alpha^{3} - \frac{25}{15} \frac{2}{5} \alpha^{4} + \dots \right)$$

$$(60)$$

We know that  $W_{1,1}$  is a linear function of  $y_1$  and  $y_2$ ; however, it is simpler to obtain an expansion directly and use (60) to verify it. For this purpose we use the equivalent contour integral for the confluent hypergeometric function,

$$\mathbf{W}_{k,m} = \frac{\alpha^k e^{-a/2}}{2\pi i} \int_{-\infty}^{\infty} \frac{\Gamma(s) \Gamma(-s - k - m + \frac{1}{2}) \Gamma(-s - k + m + \frac{1}{2})}{\Gamma(-k - m + \frac{1}{2}) \Gamma(-k + m + \frac{1}{2})} \alpha^a ds, \quad (61)$$

where the contour has loops if necessary, so that the poles of  $\Gamma(s)$  and those of  $\Gamma(-s-k-m+\frac{1}{2})$   $\Gamma(-s-k+m+\frac{1}{2})$  are on opposite sides of it. The integral can be evaluated by the method of residues. When k=m=1, the poles at which the residues have to be found are simple poles at  $s=-\frac{1}{2},-\frac{3}{2}$ , together with double poles at  $s=\frac{1}{2},\frac{3}{2},\frac{5}{2},\ldots$  The latter series gives rise to logarithmic residues. Carrying out the calculation, we obtain

$$\mathbf{W}_{1,1} = \pi^{-1/2} \alpha e^{-\alpha/2} \left( \alpha^{-3/2} + \frac{3}{2} \alpha^{-1/2} \right) - \frac{3}{4\pi} \alpha^{3/2} e^{-\alpha/2} \left\{ \log \alpha \sum_{0}^{\infty} \frac{\Gamma(p + \frac{1}{2})}{\Gamma(p+1)\Gamma(p+3)} \alpha^{p} + \frac{1}{2} \pi^{\frac{1}{2}} \left( \gamma - 2 \log 2 - \frac{3}{2} \right) + \sum_{1}^{\infty} \alpha^{p} \frac{d}{dp} \frac{\Gamma(p + \frac{1}{2})}{\Gamma(p+1)\Gamma(p+3)} \right\}, \quad (62)$$

where  $\gamma$  is Euler's constant 0.5772.... The coefficients may be put into alternative forms more suited for calculation; for instance

$$\frac{\frac{d}{dp} \frac{\Gamma(p+\frac{1}{2})}{\Gamma(p+1) \Gamma(p+3)}}{= \frac{1 \cdot 3 \cdot 5 \dots (2p-1) \pi^{\frac{1}{2}}}{2^{p} \cdot p! (p+2)!} \left\{ \gamma - 2 \log 2 + \sum_{1}^{p} \frac{1}{n(2n-1)} - \sum_{1}^{p+2} \frac{1}{n} \right\}.$$

For numerical calculation we have

$$W_{1,1} = \frac{3}{8} \pi^{-1/2} \alpha^{3/2} e^{-\alpha/2} \left\{ \frac{8}{3\alpha^2} + \frac{4}{\alpha} + \frac{3}{2} + \frac{5}{36} \alpha + \frac{11}{384} \alpha^2 + \frac{7}{1280} \alpha^8 + \dots \right\} - \left( \gamma + \log \frac{1}{4} \alpha \right) \left( 1 + \frac{1}{6} \alpha + \frac{1}{32} \alpha^2 + \frac{1}{192} \alpha^3 + \dots \right).$$
(63)

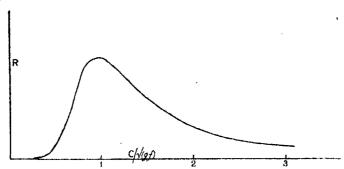
The expansion may be confirmed by comparison with the fundamental solutions of the differential equation given in (60); we find that

$$(8/3)\pi^{\frac{1}{6}}W_{1,1} = (2\log 2 - \gamma - \frac{1}{6})y_1 - y_2$$

For large values of  $\alpha$  the general asymptotic expansion of  $W_{k,m}$  is available; and in this case we have

$$W_{1,1} \sim \alpha e^{-\alpha/2} \left( 1 + \frac{3}{4} \frac{1}{\alpha} + \frac{9}{32} \frac{1}{\alpha^2} - \frac{15}{128} \frac{1}{\alpha^3} + \dots \right).$$
 (64)

9. With (63) and (64) we can now calculate the resistance R from (58). For a given depth f, the variation of the resistance with the velocity is shown in the following curve, for which R has been calculated for various values of  $o/\sqrt{(gf)}$ .



The curve is very similar in form to the two-dimensional case of a circular cylinder. For small velocities, that is  $\alpha$  large, if we take the first term of the asymptotic expansion (64), we have

$$R = \sqrt{(2\pi^3 g^7/f)} \cdot \rho a^6 e^{-5} e^{-2gf/e^2}$$

which may be compared with (30) for the cylinder. It is of interest to notice the similar law of variation of wave resistance with speed for the few cases of rigid bodies which have been worked out. The method adopted here can be applied to bodies of different forms, and it is hoped to illustrate later some interference effects.

# Problems Bearing on Residual Affinity. By Spencer Umfreville Pickering, M.A., F.R.S.

(Received June 29, 1916.)

#### [PLATE 2.]

Valency implies the existence of something equivalent to the possession by an atom of points of attachment, and is inseparable from the idea of chemical combination; but it must not be confused, as has often been done, with the force acting at those points. The properties of a mass of matter are the sum of those of its constituents, and, since molecules combine together, the affinities and valencies effecting their union must be those of the constituent atoms. The satisfaction of such additional valencies will represent a comparatively small expenditure of energy, for, even when principal valencies are concerned, as when an element forms pairs of oxides or halides, the heat evolution on combining with the additional oxygen atom is, on the average, only 38 per cent, of what it is on combining with the first atom or atoms (17 cases), and 52 per cent. in the case of the halides (10 cases).\* At this rate residual affinity must soon become reduced to a quantity insufficient for the attachment of another free atom, but might still be sufficient to unite with it if it were already in combination, and had only its own residual affinity available. Platinum is hexavalent in  $Cl_4Pt < \frac{ClK}{ClK}$ , though  $Cl_6Pt$ cannot exist. It is, therefore, only in so-called molecular compounds that the highest valencies of an atom can be expected, though no fundamental differences can be imagined between the higher and the principal valencies; this is admitted even by those who have coined a distinctive name for the higher valencies (e.g., Werner's "co-ordination values").

The general rule that additional valencies come into existence in pairs is not invalidated by certain apparent exceptions. Thus, the most stable arrangement of five atoms round a central one is two in one plane, and three in the plane at right angles; according as the positions occupied are those in the one, the other, or both planes, the atom will show valencies of 2, 3 or 5, and by the suppression or development of pairs of valencies, other values of 1, 4, 7, 9, etc., might be shown.

<sup>\*</sup> The halides of gold are exceptions, the heat of formation per halogen atom increasing with the proportion of halogen. This indicates that there is no change of valency, the aurous halides being X—Au=Au=X. The case is comparable with that of  $C_2$  combining with  $H_2$ ,  $H_4$  and  $H_6$ , where the evolution per atom of hydrogen is -23,885, -1645 and +4567, respectively.

<sup>† &#</sup>x27;Journ. Chem. Soc.,' 1893, p. 1069.

Alone of the better known elements, carbon and hydrogen appear to exhibit no higher valencies,\* and can consequently be built together to an extent unknown in other cases. This does not negative the view that carbon may sometimes exhibit a certain amount of residual affinity, sufficient to explain such facts as those observed by Thiele,† without attributing to the doubly linked atoms any additional "partial" valencies. Though Thomsen's conclusions as to the values of double and treble linkage cannot now be accepted, these doubtless represent less energy than two or three single links.‡ The existence of such multiple linkage has been contested on the ground of the inferior stability of the compounds containing them; but decomposition of a substance containing, for instance,  $\equiv C - C \equiv$  means that an advantage is gained by substituting the linkage X—C for C—C; hence, the more carbon-carbon linkages there are for such substitution, the less stable will be the compound.

Thomsen's determination of the thermal value of substituting  $\mathrm{CH_3}$  for H, when seven out of the 48 cases are omitted, is 7814 cal., the variation indicating a probable error of  $\pm$  1537 for any one value, of which, judging by the difference between duplicates, 1082 cal. is accounted for by errors of measurement, leaving only 455 for errors due to imperfect purity. Hence this value is a constant within the limits of experimental error; but it may well be questioned whether it is absolutely constant, for it varies between the wide limits of 4320 and 10,870 cal.§ (or 730 and 13,810 cal., if the seven exceptional cases are included); added to which, absolute constancy would imply that the carbon atom is, as it were, divided into four watertight compartments, the happenings in one of them being unaffected by those in the others; which is quite opposed to known facts.

With the monochloro-derivatives the constant, 2464 cal., varies between 800 and 5190, the probable error being  $\pm 1439$ , of which 1080 is attributable to measurement errors.

With radicles possessing residual affinity, such as Cl or OH, the introduction of the second unit results in an increased heat evolution, since their residual affinity can then come into play, whilst the introduction of the fourth unit results in a notable decrease, the four units then forming a ring in equilibrium round the nucleus, and being unable to draw closer to each other. The

<sup>\*</sup> The recently established combination of paraffins with soaps (loc. cit., vol. 111, p. 86) may be an instance to the contrary.

<sup>† &#</sup>x27;Annalen,' vol. 306, p. 87; vol. 308, p. 213.

<sup>1</sup> Armstrong, 'Phil. Mag.,' vol. 23, p. 73 (1887); Pickering, ibid., p. 109.

<sup>§</sup> The variation appears insignificant when the values are expressed as differences in the heat of combustion of homologues, for such differences each contain 165,809 cal., representing the heat of combustion of C and H<sub>2</sub>.

effect when the third unit is introduced cannot be predicted, and seems to vary with circumstances.

Substitution.	First.	Second.	Third.	Fourth.	Maximum difference.	Probable error.*
CH, for H						The start of the s
In CH,	6,230	5,970	6,760	4,820	1,940	$\pm 2.361$
In C <sub>2</sub> H <sub>4</sub>		6,860	7,730		2,880	$\pm 1.084$
Cl for H+	,		1		, ,, ,	
In CH4	800	16	660	- 3,080	8,880	± 858
In CoH		3,546	- 275		3,821	$\pm 1,720$
In C.H.	1	3,656	- 2,230	- 8,471	7,127	,
OOH <sub>3</sub> for H		1	1	,		
In CH.	27,020	37,730	41,350		14,330	$\pm 1,302$
CH, for H	1	1		1	1 '	, -
In NH <sub>3</sub>	- 2,927	2,600	2.570		5,527	$\pm 1,191$
CaH, for H		1	, , ,	l		,
In NH,	4,463	10,650	11,400	_	6,937	$\pm 1.851$

Table I.—Heat Evolved on the Successive Substitution of the same Radicle.

Berthelot and Ogier determined the value for CH<sub>2</sub>Cl<sub>2</sub>, but it is impossible in such a case to piece together the results of different observers using different methods.

The values for C.H., include all Thomsen's results with various hydrocarbons.

Where the element exhibiting residual affinity is in the nucleus, and the radicle introduced exhibits no residual affinity, the valency of this element may change on the first, but not on subsequent substitutions. This is so with the amines. The change of valency, which is also the explanation given by Thomsen, might be put to the test by ascertaining whether the heat of neutralisation of ammonia is 5000 or 6000 cal. less than that of the amines in the gaseous condition; for the hydrochlorides must all be similarly constituted.

Amongst the elements known to exhibit residual affinity, oxygen, nitrogen and sulphur are conspicuous. Sulphur, and the first two in the form of water and ammonia, figure in thousands of so-called molecular compounds, and their power of combining is also shown by their polymerisation, as evidenced by the exceptional heat-absorption occurring when their temperature is raised, or their state changed.\*

Metallo-Compounds.—Valency values higher than those usually exhibited seem necessary to explain the existence of organic salts of metals when in the metallo-condition, that is, when the metal forms part of a complex anion, and is, therefore, directly united to carbon, and unrecognisable by

<sup>\*</sup> Of the determinations giving the maximum difference.

<sup>†</sup> Determined directly from the heat of combustion of the compounds. Thomsen ('Untersuchungen,' IV, p. 279) adopted an indirect method, making use of certain constants which are the same in all cases, and hence reduce the apparent error. As a result, also, he got values for successive substitutions which he admits are meaningless (p. 284).

the ordinary tests, as with iron in the ferrocyanides. In 40 cases, with five different acids and 13 different metals (mostly such as are usually divalent), these isomers of the normal salts have been obtained:\* (1) by precipitation of freshly prepared solutions by alcohol, (2) by double decomposition with the organic salt of an alkali metal. They appear as emulsions, drying to amorphous powders, much more soluble than the corresponding normal crystalline salts, into which they partially and gradually change in solution. This change is accompanied by a reduction in colour-intensity, where the compounds are coloured. In many cases solutions of them may be evaporated without, or with only a partial, change into the normal salt: they then yield glassy or scaly solids. The relation between the normal and the metallo-salt in its anhydrous and hydrated condition is shown by (1), (2) and (3):

Metallo-Compounds of Alkali Metals.—Solutions of tartrate or citrate of sodium (but not of potassium) may, on repeated trials, be concentrated at 100° beyond the point (12.6 H<sub>2</sub>O for the citrate) at which crystallisation normally occurs; they then leave glassy residues, consisting approximately of Na<sub>2</sub>T,2H<sub>2</sub>O and Na<sub>3</sub>Cit,4H<sub>2</sub>O, which, over sulphuric acid, dry to scaly deposits, similar to those obtained from other metallo-compounds (fig. 1, Plate 2—fig. 2 showing the normal salt—for which we are indebted to Dr. H. B. Hutchinson). The glassy residues, exposed to air saturated with moisture, absorb water 2½ times more rapidly than do the crystallised salts of the same degree of hydration. On prolonged heating of the glassy citrate at 100°, specks of the anhydrous normal citrate make their appearance, just as in the case of some cupricompounds,† and eventually spread throughout the whole; the crystallised salt, on the other hand, cannot be dehydrated at 100°.

Ato-Compounds.—This term has been applied to substances to which the elements composing a salt have become attached—carbonato, sulphato, etc. If the substance in question is a metallo-compound, the complex would be a metallato-compound. The salt elements [formula (4), above] would occupy

<sup>\* &#</sup>x27;Journ. Chem. Soc.,' vol. 95, p. 1409; vol. 98, p. 1837; vol. 99, pp. 169, 800, 1347; vol. 101, pp. 174, 1614, 1625; vol. 103, p. 1358; vol. 105, p. 464; vol. 107, pp. 942, 955; vol. 109, p. 235.

<sup>†</sup> Loc. cit., vol. 107, p. 955.

the place of the water in the hydrated metallo-compound, which latter is really an ato-compound (hydrato). Such compounds containing  $K_2CO_8$  have been described under the name of  $\alpha$ -cupricarbonates.\* If the metal is an alkali metal they should be, and are, strongly alkaline, since they contain OM derived from a non-acidic hydroxyl (see pp. 540, 543); if the elements of an acid, instead of those of a salt, unite with the metallo-compound, the complex would be neutral.

Combination of Acids with Organic Salts.—When hydrochloric (or other) acid is added to potassium (or any other) carbonate in the presence of potassium citrate, no evolution of carbon dioxide occurs under conditions such as, in the absence of the citrate, would ensure a violent evolution of the gas. Series of seven experiments each, at 15° and 0°, in which the acid and carbonate were mixed in the presence of varying proportions of citrate, etc., in a closed flask connected with a manometer, showed that at an excess pressure of 200 mm. the following molecular proportions of carbonic acid were retained: 0.4 H<sub>2</sub>CO<sub>3</sub> by Na<sub>3</sub>Cit; 0.24 H<sub>2</sub>CO<sub>3</sub> by K<sub>3</sub>Cit; 0.08 H<sub>2</sub>CO<sub>3</sub> by NaAc; and practically none by potassium malate, tartrate and lactate. As the solubility of carbon dioxide in water was found to be reduced by potassium citrate, it must be H<sub>2</sub>CO<sub>3</sub>, and not CO<sub>2</sub>, which combines with the salt. The complexes are, naturally, unstable, and gradually decompose.

Other acids behave in the same way. The proportions required to produce a fairly well marked acid reaction in the presence of various salts at decinormal strength, using methyl orange as indicator, and subtracting from the observed values the amount required to produce the same tint in an equal volume of water, are given in Table II. With inorganic salts, the absorption

Table	II.—Equivalents	of Acid	producing	Acidity	with	One	Equivalent	of
	Alkali Metal	present, l	less that red	quired w	ith W	ater (	only.	

Acid.	Water.	KNO <sub>3</sub> .	KCl.	K <sub>2</sub> SO <sub>4</sub> .	Pot. oxal.	Pot. tart.	Pot. lact.	Pot. cit.	Sod. cit.	Pot.	Mean.
HNO,	0004	-0006	·0008	.0011	0.46	0.80	0 .64	0 57	0.31	0 .25	0.17
HC1	0004	.0000	.0000	.0010	0 .20	0.88	0.65	0.58	0.41	0.26	0 .26
H,804		.0000	.0000	0004	0 48	0.85	0.68	0.59	0.28	0.32	0.17
Oxalic	-0005	•0000	*0000	<b>*00</b> 08	0.54	0 .97	08'0	0.66	0.83	0 .83	0.22
Tartaric	0007	•0000	*0008	.0011	0.55	0.99	0.80	0.68	0.87	0.24	0.19
Lactic	.0009	10000	0012	0012	0.68	1 18	0.78	0.490	0 .83	0.88	0.19
Oitrie	0006	•0007	0000	.0007	0.80	1 '48	1 .19	1 05	0 47	0.38	0 .25
Acetic	*0016	10020	0000	·0010	1 .25	2 .39	1.78	1.85	0.63	0.55	0.29
Mean		.0005	10004	.0009	0 .22	0.83	0 .39	0 .86	0 .91	1.18	

<sup>\*</sup> Loc. cit., vol. 99, p. 800.

of acid is generally nil, except when the formation of an acid salt is possible (sulphate); with organic salts, as much as from 0·17 to 2·4 equivalents of acid are absorbed, acidity appearing gradually. These values should really be about 50 per cent. higher, for the proper degree of acidity which should be selected as indicating the point at which absorption of acid ceases is that when further additions of acid cause no further increase in acid reaction; these values were recorded, as well as those applying to the first barely discernible change of tint, but they are more difficult of determination than those for the degree of acidity selected for the values in the Table.

The combination of acids with organic salts explains why the titration of an organic acid is generally impossible: but as the neutral complex formed is always partially hydrolysed, it will show some acid reaction, and the possibility of titration will depend on the delicacy of the indicator, as well as on the nature of the acid. Thus the following results were obtained:—

Acid.	Methyl orange.	Litmus.	Phenolphthalein.
Tartarie Oxalie Acetie Lactie Citrie	23 per cent. low 32 ,, ,, 80 ,, ,, 20 ,, ,, Impossible	4 per cent. low 2 ,, ,, 20 ,, ,, 10 ,, ,, 46 ,, ,,	Correct. ,, ,10 per cent. low. 38 ,, ,,

Double Decomposition.—An ato-compound with the same salt elements in both parts of the molecule—c.g., a tartrato-tartrate—would be isomeric with the metallo and normal salts, and such ato-compounds figure in one of the four or five stages given below as occurring in double decomposition. They form jellies, or gelatinous precipitates, seen under the microscope to consist of membranous particles, illustrated in fig. 3, Plate 2, closely resembling, in miniature, the scale form of the hydrated metallo-compounds (fig. 1). They have been obtained in a dozen cases previously described.\* In many instances one or other of the following stages are passed too rapidly for recognition, and with inorganic salts it is generally only the last stage which is noticeable.

- (1) The first stage when, for instance, barium chloride is gradually added to concentrated solutions of tartrate or citrate, consists of the precipitation of bari-tartrate as an emulsion: this rapidly redissolves. In other cases, previously investigated, the emulsion was sufficiently permanent to admit of its being analysed.
  - (2) It dissolves because it forms a highly soluble ato-compound with the

excess of potassium tartrate present, and the limit up to which dissolution occurs and the precipitation next described (3) begins\* on increasing additions of the barium salt, shows that its formula must be BaT,3K<sub>2</sub>T (ratio found, Ba: 3·12 K<sub>2</sub>T); in the case of the citrate it is Ba<sub>3</sub>Cit<sub>2</sub>,3K<sub>3</sub>Cit (ratios found, Ba<sub>3</sub>: 2·95 K<sub>3</sub>Cit and Ba<sub>3</sub>: 3·1 K<sub>3</sub>Cit). [Alcohol added to these liquids precipitates the barium metallo-compound as an emulsion or solution, containing but little potassium. With the citrates, the solutions, if left for from 15 minutes to two hours, gelatinise, the jelly consisting of minute particles resembling bacteria (Plate 2, fig. 5). This contains a smaller proportion of the alkali metal citrate than that in the citrato-citrate in solution; the ratios found were 0·67-0·93 K<sub>3</sub>Cit and 0·73-1·33 Na<sub>3</sub>Cit to each Ba<sub>3</sub>Cit<sub>2</sub>. In some cases the metallato-compounds change directly into the corresponding normal double salts, and ultimately into the normal single salt;† in such an event the next stage is suppressed.]

- (3) Continuing the addition of barium chloride, a gelatinous precipitate begins to form, soon rendering the mixture semi-solid. This is a metallato-compound of membranous structure, which, on analysis, is found to contain no potassium or chlorine, and must, therefore, be isomeric with the metallo and normal salts. In solubility it is intermediate between them; the tartrato-tartrate dissolves to the extent of 0.7 grm. barium in 100 c.c. at 10°, the citrato-citrate, 0.13 grm.; the values for the normal salts are 0.096 and 0.032, respectively, whilst those for the metallo-compounds are indefinitely large.
- (4) After some hours the normal salt begins to crystallise from the liquid, the bulky metallato-compound simultaneously re-dissolving, and disappearing entirely in a day or two. If only a small layer of the metallato-compound is present, the normal salt appears as isolated crystals, each in the centre of a circular area free from ato-compound. Similar indirect changes have been followed under the microscope (loc. cit.).

Neutralisation is but a special case of double decomposition, and the addition of barium hydroxide to tartaric or citric acid yields a series of compounds precisely similar to those mentioned above. The soluble ato-compound, in the case of the tartrate, is BaT,H<sub>2</sub>T, but, in the case of the citrate, Ba<sub>2</sub>Cit<sub>2</sub>,4H<sub>2</sub>Cit. Such compounds, including the strontium analogue of this particular tartrate, have been isolated in several instances

<sup>\*</sup> The precipitate being somewhat soluble, especially in the case of the tartrate, the point at which it appears varies (in a nearly rectilinear function) with the dilution. Series of determinations, with different amounts of water present, gave the point at which it would first appear if no water were present to dissolve it.

<sup>†</sup> Loc. cit., vol. 107, p. 948.

<sup>†</sup> For the method see loc. cit., vol. 107, p. 949.

by precipitation with alcohol;\* their acid reaction is but feeble, being due merely to hydrolysis, the compounds themselves being neutral. They, too, like the potassium compounds, sometimes change into the isomeric normal salts—acid salts in this case—which are sparingly soluble and crystalline, r.g., the acid tartrates and racemates of the alkali metals, which cannot be regarded as intermediate between the highly soluble neutral salts and the acids.

Basic Metallato-compounds.—The substitution of a metallic oxide for H<sub>2</sub>O in the hydrato-compound (3), p. 536, should produce a basic or alkaline body. When concentrated tartaric acid is gradually added to baryta solution, some permanent precipitate is formed, and neutrality is attained before an equivalent of acid is reached. On dilution, the precipitate dissolves, and alkalinity reappears. With one equivalent to two of hydroxide, the precipitate approximates to 3BaT,BaO, but varies in basicity, and also in solubility (from 0·1 to 0·45 grm. Ba in 100 c.c.), with the proportions taken. No analogous reaction occurs with citric acid, but basic cobalti-malate and citrate, as well as some twenty alkaline cupri-tartrates, have been isolated,† and it has been shown that, in the case of seven metals, the initial action of an alkali on their organic salts results in forming a soluble metallo-compound with M'OH in the place of H<sub>2</sub>O.‡

Mixed Metallato-compounds.—The addition of barium chloride to mixtures of potassium citrate and sulphate results in a series of changes similar to those occurring in the absence of sulphate (p. 538), except that, when the barium reaches certain proportions, an opalescence—to be reverted to immediately—occurs before the permanent membranous precipitate forms. This latter consists of a sulphato-citrate, but, though some eighty preparations of it under different conditions were examined, no definite results as to its composition (beyond the probable existence of Ba<sub>3</sub>Cit<sub>2</sub>,3BaSO<sub>4</sub>) were obtained. The compounds possible are very numerous.§ They contain no admixed barium sulphate (though they do so in the case of the tartrate), and are gelatinous, even when the proportion of barium as sulphate to barium as citrate is 4:1; also, the proportions in the precipitates are very different from those in the solutions yielding them, and the curves representing the variation of composition with conditions show undoubted breaks. In the case of the tartrate, the precipitate contains some tartrate under conditions such that, in the absence of sulphate, no tartrate would be precipitated.

<sup>\*</sup> Loc. cit., vol. 109, p. 246.

<sup>†</sup> Loc. cit., vol. 107, p. 946; vol. 101, p. 1616.

<sup>1</sup> Loc. cit., vol. 109, p. 237.

<sup>§</sup> Cf. loc. cit., vol. 99, p. 801.

Taking varying proportions of potassium citrate and sulphate, the point at which ordinary barium sulphate makes its appearance in the membranous precipitate was determined by microscopic examination, which we owe to Dr. Hutchinson, to be  $2K_8Cit:3\pm0.3K_2SO_4$ : up to this point, therefore, there can be no free sulphate present, and it must exist as a sulphato-citrate of potassium. The formation of such compounds explains why the presence of an organic salt interferes with the quantitative precipitation of barium sulphate, etc. No definite results were obtained by adding baryta to mixtures of sulphuric acid with tartaric or citric acids.

Inorganic Metallo-compounds.—The opalescence mentioned above consists of a membranous solid like the other ato-compounds (fig. 3, Plate 2), but contains the elements of barium sulphate only, being, therefore, a sulphato-barisulphate. On filtering through a very fine porous candle, it forms a translucent jelly, which may be washed by leaving it in a dialyser for many weeks. It becomes more opaque, but retains its gelatinous, adhesive character, without changing into the normal sulphate (which is shown in fig. 4).

That inorganic salts may exist in the condition of metallo-compounds has already been suggested in reference to the modifications of the double sulphate  $\operatorname{CuK}_2(\operatorname{SO}_4)_2^*$  and of ferric chloride.† It appears, also, that in certain cases (the iodates of potassium and sodium) alcohol precipitates the salt as an emulsion from its solution.

Heat of Neutralisation.—Thomsen's results, the seeming irregularities in which lead to important conclusions, are collected in Table III. The high values for sulphuric, selenic and hydrofluoric acids are omitted; the first two are erroneous, owing to the concentration having been too great, though they cannot be corrected with sufficient accuracy for use here; there is probably a similar source of error as regards hydrofluoric acid, and also in a minor degree as regards those somewhat exceptionally high values which appear in the Table. The seven inorganic monobasic acids showing lowest values give a mean of 13,743 cal., which is practically identical with the mean (E) for the polybasic acids; the relative values in other cases, compared with this as unity, are entered in brackets.

<sup>\*</sup> Loc. cit., vol. 99, p. 811.

<sup>†</sup> Loc. cit., vol. 105, p. 480.

<sup>‡</sup> Loc. cit., vol. 55, p. 325.

Table III.—Heat of Neutralisation of Acids.

<b>A</b> cid.	lst NaOH.	2nd NaOH.	3rd NaOH.	2 NaOH.	Excess alkuli.	Alkali absorbed by salt.
I.	II.	111.	ıv.	<b>v</b> ,	V1.	VII.
HCl HBr HI HClO <sub>3</sub> HBrO <sub>3</sub> HIO <sub>3</sub> HNO <sub>5</sub> HPO <sub>3</sub> HClO <sub>4</sub> HPO <sub>2</sub> H <sub>2</sub>	13,680 13,760 13,780 13,810 13,880 14,380 14,080				10 (2) 	0 0 0 0 00012 0 00010 0 0 00026 0 00010 0 00021
Mean A	13,982 (1·017)		to describe the			
Formic Acetic Propionic Ethyl sulphonic Chloracetic Dichloracetic Trichloracetic	13,400 13,448 13,480 (0 979) 13,460 14,280				15	0 00008 0 00007 0 000020 0 0011 0 0048 0 0000
Mean B	13,831 (1 '006)				erMr. Zaktovis visa akaapus viinner ron	
Oxalic Succinic Malic Tartaric Aconitic Citric	12,400 13,085 12,442 12,848	14,484 11,756 18,198 12,872 12,983 12,778	18,333 18,537		222 (2) 228 (2) 584 (2) 581 (1) 986 (3) 3,743 (3)	0 ·00018 0 ·00201 0 ·00127 0 ·00048 0 ·00028
Monn C	12,874 (0 937)	12,984 (0 ·944)	13,435 (0.978)			
H <sub>2</sub> SO <sub>3</sub>	14,772 14,880 14,829	13,098 12,252 12,618 12,249 12,586	6,951 8,886	2. 14,484 2. 13,512 2. 13,724 2. 13,589 2. 13,790	360 (2) 460 (2) 402 (2) 1,251 (8) 1,484 (8)	0 000008*
Menn D	15,059 (1 ·096)	12,559 (0.914)	7,644 (0·557)		-au-ten <del>interess erstellen skrivering de till</del> en i l	The same of the sa

<sup>\*</sup> The sulphite is said to be strongly alkaline: when pure it is not so.

Table III—continued.

Acid.	1st NaOH.	2nd NaOH.	3rd NaOH.	2 NaOH.	Excess alkali.	Alkali absorbed by salt.
1.	II.	111.	IV.	v.	VI.	VII.
H <sub>2</sub> IH <sub>3</sub> O <sub>6</sub> * H <sub>2</sub> S <sub>2</sub> O <sub>8</sub> H <sub>2</sub> SiF <sub>5</sub> H <sub>2</sub> PtCl <sub>6</sub>	(5,150)	(21,440)		2. 13,295 2. 13,770 2. 13,310 2. 13,610	·` ´	E ages organis
Mean E				2. 13,756 (1 001)		
H <sub>4</sub> P <sub>2</sub> O <sub>7</sub> †	2. 14,822	8rd and 4th. 2. 12,047 (0.876)		4. 13,185 (0.960)		
		Abnormally	Low Values	<b>5.</b>		
HSH HClO HCN	7,738 9,980 2,770		!		64 (1)	
H <sub>2</sub> CrO <sub>4</sub> H <sub>2</sub> As <sub>2</sub> O <sub>4</sub> H <sub>2</sub> OO <sub>2</sub>	13,134 7,300 11,016	11,586 6,480 9,168			444 (2) 1,800 (2) 408 (2)	
H <sub>2</sub> B <sub>2</sub> O <sub>4</sub>	11,101 4,816	8,909 914 670			630 (4) 182 (2) 5,450	

<sup>\*</sup> The anomalous behaviour is explained by Thomsen by the existence of two acids,  $H_4I_2H_6O_{12}$  and  $H_2IH_3O_6$ .

Alkalinity of Salts of the Alkali and Alkaline Earth Metals.—If the organic salts of these metals exist partially in solution as metallo-compounds, the latter would unite with molecules of the normal salts, producing metallato-compounds (tartrato-tartrates, etc.), containing non-acidic hydroxyl with H displaced by K, etc., which, as in every other known case, would result in alkalinity. The alkalinity of organic salts is well known, and, as will be shown, cannot be explained by hydrolysis; but it is not so well known that a similar, though much feebler, alkalinity characterises all the so-called neutral inorganic salts of these metals. Table IV contains the results obtained at 70°, using well boiled water with pure litmus as indicator; the alkalinity is also recognisable with methyl orange slightly tinted with acid, and in some cases with phenolphthalein. In the cases marked \* the salt was purified by repeated crystallisation, or precipitation by alcohol, in platinum.

<sup>†</sup> The values for the 3rd and 4th NaOH were not determined separately.

Results with a few organic salts are added for comparison. With these, the alkalinity increases with rise of temperature; with the inorganic salts, in six cases examined, there was no appreciable, or a barely appreciable, alteration in tint on cooling to  $10^{\circ}$ .

Table IV.—Alkalinity in Equivalents × 10<sup>5</sup> of a Gramme-Equivalent (or in brackets, a Gramme-Molecule) of Salt when Dissolved in 10 litres of Water.

Salt.	К.	Na.	Li.	Ca.	Sr.	Ba.	Mg.
Chloride	44*	58*	31*	72 (74)	115 (87)	88 (74)	136 (118)
Bromide	42	57	58*				
Iodide	29*	46*		! Ì			
Chlorate	29	50					
Bromate	48*	64*	-	i i			
Iodate	45*	80*	****			*****	
Nitrate	83	53	40*	85 (107)	88 (88)	112 (116)	145 (169
Perchlorate	48	59		`´		` ´	`
Sulphate	64 <b>*</b> (55*)	70 <b>*</b> (66*)	48* (50*)				69 (81)
Sulphite	`29#	`	`'			,	
Thiosulphate	64*	87 (98)		_		_	
Oxalate	108 (288)	`'				-	
Tartrate	`141´ (278)	149 (197)				· <del>-</del>	
Citrate	3100 (9940)	2706 (9356)	(3806)				
Acctate	`8140´		`′				

The alkalinity of inorganic salts is roughly proportional to the dilution, that of a gramme-molecule and gramme-equivalent, each in 10 litres, being approximately the same; and this rough proportionality may extend over a considerable range of dilution, as the following values (p. 545) with sodium sulphate and potassium chloride show; but the increase in alkalinity slackens with extreme dilution, and also, in the case of sodium sulphate, disappears altogether with extreme concentration.

With organic salts, the alkalinity for the two concentrations given in Table IV is generally constant, but at high concentrations it decreases considerably, as with sodium sulphate.

That this alkalinity is due to loss of acid in the preparation of the salt is disproved by the results with sodium sulphate, also by the fact that potassium chloride gave constant values,  $42-46 \times 10^{-5}$ , when (a) washed with water, and dried without heating, (b) twice precipitated by alcohol, and similarly dried, (c) treated in this way twice again, (d) acidified, and twice

precipitated,	(e)	twice	dissolved,	evaporated,	and	heated	for	eight	houre
at 100°.									

Volume	1 Na	±8O⁴.	K	Cl.	, кл.		
containing one equivalent.	Alkalinity.	Alkalinity Volume	Alkalinity.	Alkalinity Volume	Alkalinity.	Alkalinity Volume	
litres.							
0.09	0	0	1		·	4.pp. 4	
0.18	1	5.5	1.1	6 · 1	11.5	64	
0.36	4	11.0	2.2	5 - 9	13.7	36	
0.72	6	8.3	3.6	5.0	16.9	23	
I :26	11	8 .0	4.8	5.8	19.9	16	
2 .56	18	0۰ 7	17	6.6	28	11	
12.6	78	6 · 2	4.5	3 · 6	56	4.4	
32 .5	130	4.0	85	$2 \cdot 7$	116	3 ·6	
82 .5	270	8.8	236	2.8	170	2 · 1	
132 · 5	350	2 ·6	275	2.0	180	1 .8	

That some salts may be hydrolysed in solution is not questioned, but if this is to account for their alkalinity, some evidence of it should exist in the heat of neutralisation values, for hydrolysis is reversed neutralisation, and it should be much more marked with the strongly alkaline organic, than with inorganic salts. The heat of neutralisation, it is true, is somewhat less in the former than in the latter case, but this is explicable on other grounds (p. 547), and the deficit bears no relation to the alkalinity of the salt: thus:—

	Acetate.	Citrate.	Tartrate.	Oxalate.
Deficit of heat of neutralisation	-343 cal.	-749 cal.	-1086 cal.	+ 396 cal.
Alkalinity of salt	0 .08140	0.08100	0 00141	0.00108

Moreover, if hydrolysis occurs, it will increase, and the heat of neutralisation decrease, as the proportion of base to acid is altered up to the point of equivalence. This is the case with the admittedly weak acids entered at the bottom of Table III (see also the rapidly diminishing values obtained by Thomsen on adding successive fractions of 1NaOH to silicic and boric acids); but no such decrease, indeed, a slight increase, is observed with the majority of organic acids (mean C, Table III), though their salts are strongly alkaline.

Whether hydrolysis occurs or not, it cannot account for alkalinity, unless the alkali affects the indicator more powerfully than does the acid. According to the conductivity and other properties, it should not do so in certain cases where alkalinity is conspicuous, for even in comparatively strong solutions, hydrochloric and nitric acids, potash and soda, are all equally, and nearly entirely, ionised.\*

That acids and alkalis affect indicators equally, was proved by determining the minimum quantities recognisable by means of litmus, the observer being kept in ignorance as to which of the two tubes had had the reagent added to it. The acids examined were sulphuric, hydrochloric, nitric, oxalic, tartaric, citric, acetic and malic; the bases, potash, soda, lithia, lime, baryta and ammonia. In one series they all gave the limit as 1 to  $2 \times 10^{-6}$  equivalent per 100 c.c., in another 1 to  $2 \times 10^{-5}$  (dilutions of 1 equivalent in 700,000) and 70,000 litres, respectively): the reaction with the litmus being quantitative, the delicacy is increased by reducing the intensity of the coloration. With the faintest possible coloration, sulphuric, hydrochloric, citric and acetic acids all gave the limit as 2 to  $4 \times 10^{-7}$  (dilution, 3,500,000 litres), and with the strongest workable coloration,  $6 \times 10^{-5}$  (dilution, 17,000 litres), except acetic acid, which gave  $8 \times 10^{-6}$ . Slightly reddened methyl orange gave for these, and for oxalic and tartaric acids, and for potash and ammonia, 1 to  $2 \times 10^{-5}$ , acetic acid giving 2 to  $4 \times 10^{-5}$ . These dilutions embrace those of the alkali present in inorganic salts, which is about 20,000 litres in the values in Table IV, up to 180,000 litres in those given on p. 545.

Acids, Bases, and Salts.—Acidity is conditional in organic acids, where our knowledge of constitution is soundest, on the presence of an hydroxyl side by side with a doubly bound oxygen atom. It is inconceivable that what is essential in this case should be immaterial in any other. It is equally inconceivable that this doubly bound oxygen atom, essential to acidity, should play no part in neutralisation. The neutralisation equation,

## R'OH + HOM' = R'OM' + HOH

represents the action as being a double decomposition of the simplest character—an interchange between H and M' of union with one atom of oxygen for union with another—and should evolve no heat except that entailed in the conversion of a free molecule of water into part of a mass of liquid water, which is 8900 cal. at 18°. But the action cannot be a case of double decomposition, for it is not reversible, except in certain instances, and the heat evolved in it is 13,743 cal. Clearly, some affinity, not represented by this equation, becomes satisfied; this must be the residual affinity of the doubly bound oxygen atom, brought into play by the

<sup>\*</sup> Noyes, 'J. Amer. Chem. Soc.,' vol. 30, p. 345 (1908). The weakness of an acid or alkali in its action on an indicator is attributed, on the dissociation hypothesis, to its not being broken up into ions. A more obvious explanation is that it is not present as acid or alkali, but as anhydride, demonstrably so in such cases as CO<sub>2</sub>, H<sub>2</sub>S, H<sub>2</sub>N, HCN.

substitution of a metal possessing residual affinity, for hydrogen possessing none, the linkage in a normal salt being (1), or, more probably, (2),\*

(1) 
$$\mathbb{R} \stackrel{O}{\rightleftharpoons} \mathbb{N}_{\mathbf{a}}$$
 (2)  $\mathbb{R} \stackrel{O}{\rightleftharpoons} \mathbb{N}_{\mathbf{a}}$  (3)  $\mathbb{R} \stackrel{O}{\rightleftharpoons} \mathbb{N}_{\mathbf{a}}$  (4)  $\mathbb{R} \stackrel{O}{\rightleftharpoons} \mathbb{N}_{\mathbf{a}}$  (5)  $\mathbb{R}_{\mathbf{a}} \stackrel{O}{\rightleftharpoons} \mathbb{N}_{\mathbf{a}}$ 

It is known that the halide acids owe their acidity to the presence of water, and the present view will necessitate their containing the elements of 2H<sub>2</sub>O, e.g., H<sub>4</sub>ClOOH; † an additional H<sub>2</sub>O must also be assigned to a few other acids. The alkalinity of the salts is an important argument for the presence of two atoms of oxygen, for, being inexplicable on other grounds, it proves the presence of small quantities of ato-compounds. The halogens consequently must act as heptads, sulphur, etc., as octads in the sulphites (both already advocated by others on different grounds), and phosphorus, etc., as nonads in the phosphites; in all cases three stages beyond the lowest valencies.

The metallo-compound, with the higher valencies operating, will be depicted by the above formula (3), or, more probably, by the duplicated formula (4), which harmonises better with (2) (p. 536), and, as either of these represents a smaller number of valencies in operation than in the normal salt, it will agree with the fact (which the simpler formulæ on p. 536 did not) that the metallo-compound is the less stable of the two, as evidenced by its spontaneous transformation into the normal salt, and by the heat of neutralisation of organic acids, where the proportion of metallo-compound formed is large, being less than that of inorganic acids; the difference, taking the more uniform results (Table III, p. 542), is 2 per cent., or, taking all the results (means A and B), 1 per cent.

An acid salt might be intermediate between the acid itself and the neutral salt, but it certainly is not, for, whilst the full heat of neutralisation of a dibasic inorganic acid is strictly normal, there is a difference of 18 per cent. in the heat evolved by the two equivalents of base (Table III, mean D). On the dissociation hypothesis, neutralisation involves no

- \* We must suppose that higher valencies do not come into operation when the same compound could exist without their doing so. If the normal salt were  $R < \bigcirc_{0 = Na}^{O}$ , no rile could be assigned to the doubly linked oxygen in neutralisation, and an acid salt would be exactly intermediate between the neutral salt and the acid, which it is not (vide infra).
- † This does not negative the existence of some of the simple halide, HCl, in the solution. The remarkable colour changes of the copper and ferric halides (loc. cit., vol. 105, p. 469) on dissolution and dilution show that they must exist in two fundamentally different conditions.

change but the deionisation of H and OH, and such a difference is impossible: but, on the present view, it can be explained, as shown in formula (5), by the residual valency of the other oxygen atoms, instead of that of the doubly bound oxygen, operating in the acid salt. But organic acids do not form acid salts in solution (p. 540), hence there is no such inequality in the successive addition of equivalents of base in their case (mean C); the first equivalent neutralises half the acid entirely, the metallo-compound uniting with the other half to form a metallato-compound; the second equivalent then neutralises the rest of the acid contained in this, and another metallato-compound, containing the elements of the normal salt, is formed. The reaction of both equivalents of base is the same, except for any small differences in the heat of formation of the two metallato-compounds from their proximate constituents, hence the successive evolutions of heat are nearly the same.

Without assigning an unacceptably high valency to phosphorus and arsenic, phosphoric and arsenic acids must be dibasic only, and they evidently are so, for a third equivalent of base evolves only half the normal heat, and the compounds formed are strongly alkaline. But pyrophosphoric acid might be tetrabasic, in spite of its containing only seven atoms of

oxygen, the linkage of three of the oxygen atoms being 
$$=0$$
  $0$   $=$   $Na$   $=$   $Na$ 

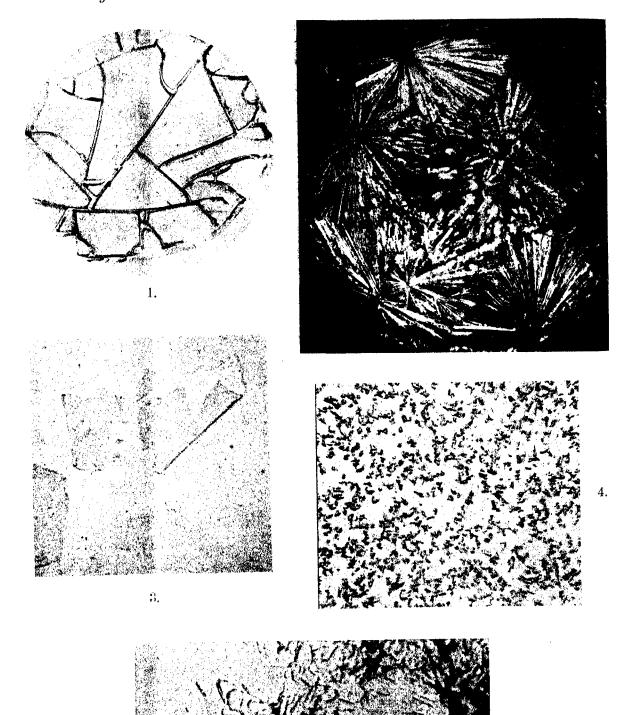
and the heat of neutralisation shows it to be so; it acts like a double molecule of a dibasic acid.

Since carbon exhibits no valency higher than 4, carbonic acid must be monobasic, and, certainly, bodies such as Na<sub>2</sub>CO<sub>3</sub> cannot be termed salts—the product of the neutralisation of an acid—for they are strongly alkaline, and alkalinity implies reversibility of the action by which Na has been substituted for H in the OH; hence this hydroxyl cannot have been an acidic hydroxyl.\* Addition of excess of alkali (excess being necessary with a reversible reaction) in such a case should evolve 8900 cal.; and, with one acidic and one non-acidic hydroxyl, as in carbonic acid, the evolution should be 22,643 cal.; this agrees approximately with the total of 20,592 evolved with a limited excess (Table III): boric acid gives 20,640 cal.† In all these

<sup>\*</sup> Subsequent investigation has showed that the molecular alkalinity of K<sub>2</sub>CO<sub>3</sub> and KOH is the same; hence both molecules must contain one "alkaline" potassium atom.

<sup>†</sup> The lowness of the value for the first equivalent of alkali proves the existence of some hydrolysis, even as regards the acidic hydroxyl. With chromic acid the values are nearly normal for both hydroxyls.

5.



cases of low values, the acids themselves are non-existent as definite compounds, and the so-called salts are strongly alkaline.

Little attention has ever been directed to the fact that alkalis combine with normal salts, evolving often a considerable amount of heat. Thomsen's values are given in Column VI (Table III), the numbers in brackets being the equivalents of alkali added; these have been supplemented (Col. VII) by determining the equivalents of alkali which must be added to the potassium salts before a definite alkalinity is produced, using the same method as that for investigating the combination of acids with salts (p. 537). This combination implies the conversion of R=0 into  $R< {\rm OH} \over {\rm OK}$ , the compounds formed being analogues of basic salts.

It is possible to estimate roughly whether the satisfaction of the residual affinities coming into operation according to the present views will account for the actual magnitude of the heat of neutralisation. To do so, it must be assumed, doubtless incorrectly, that the heat evolved on the satisfaction of each auxiliary valency is the same in every case, and that, with organic salts the product is entirely the metallato-compound, and with inorganic salts The differences between the heats of neutralisation of these two classes of acids, in the case of those which are mono- and poly-basic, gives 590 and 1756 cal., respectively (mean, 1,173 cal.), as the evolution on the satisfaction of one additional auxiliary valency [cf. formulæ (2) and (4), (p. 547)], so that in the formation of a normal salt, where three such valencies become saturated, (2), there would be an evolution of 3519 cal., which, with the heat evolved on the condensation of the water molecule, would give 12,419 cal., against the observed normal heat of neutralisation, 13,743 cal. A closer agreement could not be expected under the circumstances.

#### DESCRIPTION OF PLATE.

- 1. Soditartrate. × 15 diam.
- 2. Sodium Tartrate. ×15 diam.
- 3. Barium Sulphato-sulphate. × 300 diam.
- 4. Barium Sulphate. ×300 diam.
- 5. Potassium Citrato-baricitrate. × 300 diam.

The Theory of Decay in Radioactive Luminous Compounds.

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(Communicated by R. T. Glazebrook, F.R.S. Received May 14, 1917.)

(From the National Physical Laboratory.)

## 1. Synopsis.

It has been found\* that the luminosity of radium luminous compound at first rises rapidly to a maximum and then decreases, according to an exponential law, for about 200 days from manufacture. From this time on, however, the rate of luminosity decrease becomes slower and slower, so that the brightness tends to approach a limiting value which is not zero.

The following paper is the result of an attempt to find some explanation of this behaviour such as will furnish grounds for the prediction of the ultimate behaviour of compounds of varying composition. The theory of destruction of "active centres," put forward by Rutherford to explain the fact of decay,† leads to a simple exponential which, as has been said, represents the results to a sufficiently close approximation during the first part of the life, but fails increasingly at the later period.

To represent fully the complete luminosity curve it is necessary to assume some factor operating in a direction opposite to that of destruction of the active centres.

It is shown that the observed results are well represented by the expression found on the assumption that the destroyed active centres recover at a rate proportional to their concentration in the material. This rate is termed for convenience "the rate of recovery," but, without further extended investigation of the nature of the supposititious active centres, the term can only be justified as a convenient method of representing the observed facts, and cannot be regarded as having any basis in our knowledge of the mechanism of the luminosity of radioactive luminous compound.

Two applications of the "recovery" theory are given: (i) The investigation of the ultimate luminosities of compounds containing different proportions of radium in samples of zinc sulphide of the same characteristics. This is of importance in considering the most suitable radium content to employ for any specific purpose. (ii) The calculation of the total light emitted by a sample of radium luminous compound during any portion of its life.

<sup>\* &#</sup>x27;An Investigation of Radium Luminous Compound,' Paterson, Walsh, and Higgins, 'Phys. Soc. Proc.,' vol. 4, p. 215 (1917).

<sup>† &#</sup>x27;Roy. Soc. Proc.,' A, vol. 83, p. 561 (1910).

An appendix deals with the results to be expected (on the theory of recovery) from samples of mesotherium luminous compounds in which the age of the mesotherium may be from 6 months to 2 years.

## 2. Introductory.

It has long been known that the luminosity of radium luminous compounds decreases with lapse of time, and in 1910 Marsden\* made measurements of this effect in the case of zinc sulphide, willemite, and barium platinocyanide acted on by radium emanation. His source of radiation was, of course, decaying, but he found that the decay of luminosity of the luminescent substance was, in all cases, more rapid than that of the source of the radiation.

Rutherford (*loc. cit.*), in a paper which accompanied Marsden's, put forward a theory to account for the results observed by Marsden. He suggested that each  $\alpha$ -particle emitted by the radioactive agent collided with a number of active centres in the luminescent substance, each collision causing a flash of light, and the destruction of the active centre. Thus the scintillation due to a single  $\alpha$ -particle would be made up of a number of individual flashes each signifying the destruction of one active centre.

It is clear on this theory that the luminosity will gradually decrease as the number of active centres is diminished by the continual action of the  $\alpha$ -particles, and that the decrease of luminosity will be exponential in the special case of a radioactive agent of constant  $\alpha$ -ray activity, so that the brightness at any time is given by  $B = ce^t$ , where c is a constant.

The object of the following paper is to examine the applicability of this theory to the results obtained on samples of radium luminous compound studied over the course of a year at the National Physical Laboratory (loc. cit.).

Since practically the whole of the luminosity of a radium compound is due to  $\alpha$ -particles with their recoil atoms, it will be clear that the only products of importance are the radium itself, the emanation, radium A, and radium C, since these are the only products giving  $\alpha$ -particles with the exception of polonium, the effect of which, in the case of compound made up from freshly prepared radium, will be negligible at least for the first two years, owing to the long half-transformation period of the intermediate product radium D. This is shown by the following Table, which gives the percentage of radium F present during the first five years of life of freshly prepared radium:—

<sup>\* &</sup>quot;The Phosphorescence produced by the α- and β-Rays," E. Marsden, 'Roye Soc. Proc.,' A, vol. 83, p. 548 (1910).

Period (years).	Amount of RaF present (percentage of Ra present).	a-Ray activity of the RaF present (percentage of Ra- activity.	Ions produced by Rak (percentage of Ra and products).
0.6	0.00014	9.75	0.16
1.0	0.00042	2 · 26	0.49
1 .2	0.00075	4.08	0.88
2.0	0.00110	5 .92	1 .29
3.0	0 .00180	9 .68	2.10
5.0	0.00314	16 -9	3 .67

Table I.

The second column gives the number of atoms of radium F present, expressed as a percentage of the number of atoms of radium present, while the third column gives the number of  $\alpha$ -particles due to the RaF present, expressed as a percentage of the number emitted by the radium present. The figures of column 4 represent the ionising powers of the RaF present, expressed as a percentage of the corresponding ionising power of the radium present, together with its products as far as radium 1).

Now for practical purposes it may be assumed that the transformations of RaA, RaB, and RaC take place practically simultaneously with the transformation of the emanation, so that in new radium initially free from emanation, the growth of the emanation is accompanied by a rise in  $\alpha$ -ray activity such as would be caused if each atom of emanation, in its transformation, gave rise to three  $\alpha$ -particles producing  $1.74 \times 10^5$ ,  $1.88 \times 10^5$ , and  $2.37 \times 10^5$  ions respectively.\*

Hence if, as in Rutherford's theory, we suppose that the luminosity produced by an  $\alpha$ -particle is, other conditions being the same, very nearly proportional to the number of ions it is capable of producing,† we may regard each atom of emanation as responsible for, very approximately, four times the effect of an atom of radium alone which produces  $1.5 \times 10^5$  ions.

From this it is clear that when the emanation has attained equilibrium in a sample of luminous compound about one-fifth of the luminosity of the compound will be accounted for by the a-rays from the radium, and four-fifths by those from the emanation and its products. Calling this equilibrium amount unity, the amount of emanation present at any time t after the compound has been prepared (with radium absolutely free from emanation) is given by  $(1-e^{-\lambda t})$ , where  $\lambda = 0.180$  and t is expressed in days. The values of this function show that the amount of emanation present has

<sup>\*</sup> Rutherford, 'Radioactive Substances and their Radiations,' p. 164.

<sup>†</sup> Loc. oit., p. 510.

attained its equilibrium value to within 0.1 per cent. in a period of 50 days from the beginning.

Thus the rate of production of  $\alpha$ -particles at any time t from the period at which the radium was free from emanation is given by the formula  $R[1+3(1-e^{-\lambda t})]$ , where R is the rate of production from the radium alone. In the same way, taking into account the different ionising powers of the various  $\alpha$ -particles, the rate of production of light is given by  $R[1+p(1-e^{-\lambda t})]$ , where p is very nearly 4, and R is now the rate of production of light from the radium alone.

With this expression for the activity of the  $\alpha$ -radiation, we will now consider the variation with time of the luminosity of a sample of freshly prepared radium luminous compound.

# 3. Examination of Rutherford's Theory, involving Exponential Decay of the Luminosity.

Let us suppose that in a given sample of radium compound the number of active centres present at time t after preparation is n.

The number destroyed in time dt is, let us suppose, dn, and this is proportional to (i) the number of active centres present, n; (ii) the rate of production of  $\alpha$ -particles, taking into account the several ionising powers of each; (iii) the length of time during which the bombardment takes place, dt.

Hence 
$$dn = -kn[1+p(1-e^{-\lambda t})]dt, \tag{1}$$

where k is an arbitrary positive constant depending on the units adopted for n and t, and, possibly, on the composition of the zinc sulphide.

It is assumed that the light emitted is proportional to the number of active centres destroyed, each centre giving on the average a definite fraction of a candle-hour at the instant of destruction. The brightness B, however, is proportional to the rate of destruction of the active centres, so that

$$B_t = -cdn/dt = ckn[1 + p(1 - e^{-\lambda t})],$$
 (2)

where c is a constant relating the rate of destruction of the active centres with the brightness of the compound. Hence we have a simple expression for the brightness at any period of the life, expressed in terms of the initial brightness, for

$$\log_{\bullet} B_{t}/B_{0} = \log_{\bullet} [1 + p(1 - e^{-\lambda t})] - k[(p+1)t - p(1 - e^{-\lambda t})/\lambda].$$
 (3)

Now it will be clear a priori that after the lapse of 50 days, the emanation having attained its equilibrium value, this equation will have the form

$$\log_{\epsilon} B_t/B_{\theta} = \log_{\epsilon} (1+p) - k[(1+p)t - p/\lambda].$$

Hence if Bo' represent the initial brightness which the compound would have

if made up with radium already in equilibrium with its disintegration products,

$$\log_{\epsilon} B_0'/B_0 = \log_{\epsilon} (1+p) + kp/\lambda,$$
therefore,
$$\log_{\epsilon} B_t/B_0' = -k(1+p)t = -k't,$$
where
$$k' = k(1+p).$$
(4)

It will be noticed that it is not possible to find the values of p and k, but only of the product (1+p)k, from this equilibrium portion of the curve. The value assigned to p will only affect the initial value (up to 50 days), and for the purpose of calculating the earlier portions of the curves shown in fig. 1, p has been assumed equal to 4 (see p. 555).\* Further, it will be clear that a concentration of active deposit on the walls of the glass containing vessels will produce an enhanced luminosity at the surfaces measured. But again, once equilibrium in this respect has been attained, the only result will be an alteration in the value of k', not a distortion of the form of the curve.

To test the validity of equations 3 and 4, an example will be taken from the samples of compound of which the decay of luminosity was experimentally determined. Sample 3 was measured from within two days of mixing the radium with the zinc sulphide. If we first determine the constants from the values of luminosity obtained for a short section only of the life, say, between 50 and 200 days, it is found that the best value of k' is  $0.00585 \text{ (day)}^{-1}$  and of  $B_0'$  0.0495 ft. candle. The probable departure of a single observation from the value given by equation 4 with these values of the constants is found to be 4.1 per cent., which is slightly outside the estimated experimental accuracy (3 per cent. to 4 per cent.).

If, however, the most probable values of the constants be found from all the observations between 50 and 500 days, the new values are

$$k' = 0.00303$$
 and  $B_0' = 0.0336$ .

The probable departure of a single observation from the calculated value found with these constants is 7.8 per cent.

The luminosity curves obtained by substituting these two sets of constants in equations 3 and 4 are shown graphically in fig. 1 by the chain curve and the broken line respectively. The observed values are indicated by the points. It will be seen that neither curve is of the shape required for satisfactory agreement with the observed results over an extended period, although good agreement over short periods of 100 to 150 days can be

<sup>\*</sup> From the first seven observations on sample 8 (made up by a solution method) the most probable value of p was found to be 4.13.

<sup>†</sup> Paterson, Walsh and Higgins, loc. cit.

obtained. A precisely similar effect was exhibited by all the other specimens examined.

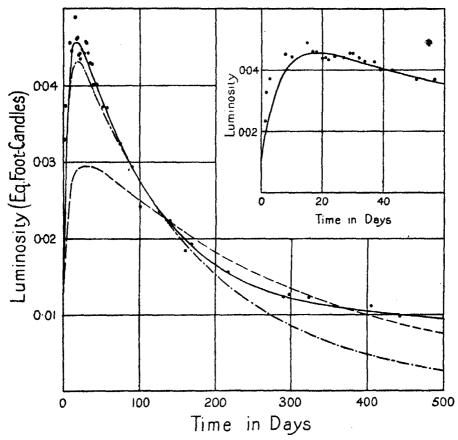


Fig. 1.—Diagram showing, for sample 3, the difference between the observed values of luminosity and the logarithmic curves  $\log B_t = kt$  (chain curve and broken line); and the agreement between these values and the curve calculated on the theory of recovery (full line).

#### 4. The Theory of Recovery.

The departure of the observed values of luminosity from the logarithmic curve cannot be explained by supposing that the active centres are of more than one kind, with different rates of decay, for the sum of any number of expressions of the form  $\frac{1}{k} \log B_t/B_0$  is an expression of the same form. Further, it may be shown that the observed luminosity curve cannot be satisfactorily explained on the assumption that the radium from which the compound was prepared contained a proportion of the long period radium D,

so that it is necessary to find some other explanation for the form of the observed curve.

It is assumed in the original theory examined above that an active centre, once struck by an α-particle with the emission of light, becomes of no further use from the point of view of luminescence. In other words, there is no recovery of the active centres.

But now let us suppose that the active centres which have been used in this way commence to recover according to an exponential law, i.e. if  $n_0$  be the number of active centres initially present, and n the number present at any subsequent time, then the rate of recovery of the active centres will be proportional to the number of extinct centres, i.e. to  $(n_0-n)$ . We may deduce, on this assumption, a new expression for the luminosity of radium compound, allowing for (i) the growth of the  $\alpha$ -radiation; (ii) the destruction of the active centres in the zinc sulphide under the action of the  $\alpha$ -rays; and (iii) the gradual recovery, according to an exponential law, of the destroyed active centres. With the same notation as before, we have that the number of active centres destroyed in time dt by the action of the  $\alpha$ -rays is  $k[1+p(1-e^{-\lambda t})]n dt$ . Also, the number restored in the same time is  $l(n_0-n)dt$ , where l may be termed the "recovery coefficient"; hence the net rate of decrease in the number of active centres is

$$dn/dt = -kn[1 + p(1 - e^{-\lambda t})] + l(n_0 - n).$$
 (5)

Now as in equation (2)

$$B_t = ckn[1 + p(1 - e^{-\lambda t})]$$
 and  $B_0 = ckn_0$ .

Hence the above equation reduces to

$$dB_t/dt + B_t[kf + l - (p\lambda/f)e^{-\lambda t}] = lfB_0,$$

$$f \equiv 1 + p(1 - e^{-\lambda t}).$$
(6)

where

The solution of this equation is

$$(B_t/f)e^r = lB_0 \int e^r dt + AB_0$$

where A is the constant of integration (found by the condition that when t = 0,  $B_t = B_0$ ), and  $r \equiv (k'+l)t + (pk/\lambda)e^{-\lambda t}$ . The expression under the sign of integration becomes integrable after expansion, so that the solution becomes

$$\begin{split} \frac{\mathbf{B}_{t}e^{r}}{f} &= l\mathbf{B}_{0} \bigg[ \frac{e^{(k'+l)}}{k'+l} + \left(\frac{pk}{\lambda}\right) \frac{e^{(k'+l-\lambda)t}}{(k'+l-\lambda)} + \dots \\ & \dots + \left(\frac{pk}{\lambda}\right)^{s} \cdot \frac{1}{s!} \cdot \frac{e^{(k'+l-s\lambda)}}{(k'+l-s\lambda)} + \dots \bigg] + \mathbf{A}\mathbf{B}_{\theta}, \end{split}$$
 where 
$$\mathbf{A} &= e^{pk/\lambda} - l \left[ \frac{1}{k'+l} + \left(\frac{pk}{\lambda}\right) \cdot \frac{1}{(k'+l-\lambda)} + \dots \right],$$

so that

$$\frac{\mathbf{B}_{t}e^{r}}{\mathbf{B}_{0}f} = e^{pk/\lambda} - l \left[ \frac{1 - e^{(k'+l)t}}{(k'+l)} + \left(\frac{pk}{\lambda}\right) \cdot \frac{1 - e^{(k'+l-\lambda)t}}{(k'+l-\lambda)} + \dots \right] - \dots + \left(\frac{pk}{\lambda}\right)^{s} \cdot \frac{1}{s!} \cdot \frac{1 - e^{(k'+l-s\lambda)t}}{(k'+l-s\lambda)} + \dots \right].$$
(7)

This equation does not readily lend itself to a determination of the constants k' and l, even supposing p known accurately, and hence we must use the simpler form of equation applicable for values of t above 50 days, viz.,

$$dB_t/dt + B_t(k'+l) = lB_0',$$

where B<sub>0</sub>' is a fictitious value of B<sub>0</sub> and is the initial brightness which the compound would have had if it had been made up with radium already in equilibrium with its disintegration products.

This equation gives as its solution

$$\log_{\bullet} \left[ \frac{(k'+l) B_t - l B_0'}{k' B_0'} \right] = -(k'+l) t, \tag{8}$$

which shows that if  $\log(B_t - m)$  be plotted against t the result will be a straight line if  $m = lB_0'/(k' + l)$ .

The close agreement between this conclusion and actual observation is shown in fig. 2, in which is plotted  $\log_{10}(B_t-0.0092)$  against t for sample 3 of compound. From the intercept of the line in this diagram on the axis of y it is seen that

$$\log_{10} \left( \mathbf{B_0'} - 0.0092 \right) = \overline{2}.650$$

so that

$$B_0' = 0.0539$$
,

and since

$$0.0092 = m = \frac{0.0539}{1 + k'/l'}$$

therefore

$$k'/l = 4.86.$$

Substituting these values in equation (8) above, we have

$$\log_{\epsilon} \left[ 22.37 \, B_{t} - 0.2057 \right] = -k' (1.2057) t.$$

Reading off the curve in fig. 2 we find that  $B_{100} = 0.027_6$ , which, on substitution in the above equation, gives k' = 0.00732, so that  $l = 0.00150_6$ . It will be seen that once the diagram shown in fig. 2 is drawn it becomes easier to deduce the theoretical values of luminosity from 50 days onwards by reading off the curve than by calculation from the formula. For the first 50 days, however, the full equation 7 must be employed. In this way we may calculate the values of brightness throughout the life of the sample

(assuming p=4), and thus obtain the full-line curve shown in fig. 1. The inset shows the values obtained for the first three months after mixing.\*

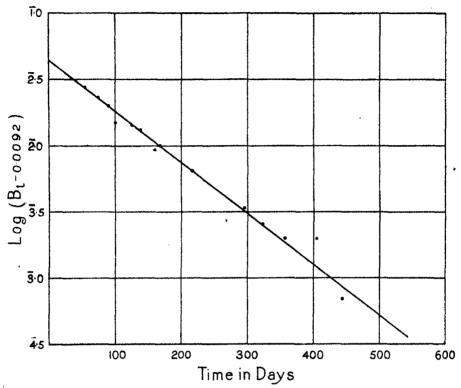


Fig. 2.—Curve showing the agreement between the observed values of luminosity and the relationship  $\log (B_t - m) = kt$ .

It will be seen that the agreement with the observed points is very close and considerably greater than that given by any logarithmic of the simpler form  $\log B_t = -kt$ . The probable error of a single observation is in this case only 3.4 per cent. At the same time, as has been said before, the agreement between the results given by the two formulæ over a limited range of 100 to 150 days is well within the error of experiment, so that it is necessary to make observations over extended periods in order to determine the true form of the curve and the values of k' and l. The curves calculated for the above sample of compound are shown, together with the observed values, in

\* A sample mixed by a solution method (where the probability of residual emanation is much less) gave results in considerably closer agreement with the theoretical curve for the first 20 days. (See Paterson, Walsh, and Higgins, loc. cit., sample 8. fig. 8.) This sample was not chosen for examination in this paper since the observations on it have not extended over so long a period.

fig. 1, where the broken lines represent the logarithmics and the full line the curve obtained by the use of the recovery factor.

It may be mentioned again that the term "recovery" as used above is not intended to imply any knowledge of the mechanism of the action tending to retard the luminosity decay of a compound. It is simply employed as a convenient expression of a conception which, in conjunction with the "active centre" theory of Rutherford, will serve to give a relation capable of expressing the observed experimental results, and hence of predicting, as in what follows, the behaviour of compounds as yet not subjected to experimental investigation.

In the following Table are given the values of the constants m, k', l and  $B_0'$  for each of the samples of compound on which observations have been made:—

Sample.	Radium		tants,		
	content.	$m \times 10^4$ .	k' × 10⁵.	$l \times 10^5$ .	$B_0' \times 10^5$
***************************************	mgrm./grm.	A transmission of the Company of the		The second secon	
1	0.32	80	550	113	47
2	0.17	68	315	117	25
8	0.35	92	730	151	54
6	0.35	65	475	88	42
7	0.85	60	480	106	33
8	0.35	110	795	219	51
9	0.84	77	980	194	47
10	0.52	77	1005	170	5-4

Table II.

The experiments on samples 4 and 5 have not extended over a sufficiently long period to allow of a satisfactory determination of the constants of these samples.

The variations to be observed above in the values of the constants for the different samples are to be ascribed to the different grades of zinc sulphide used by the various makers, or by the same maker at different times. Only samples 1 and 2 were known to have been made from the same grade of sulphide.

Two interesting applications of the theory described above are as follows:-

(1) From the diagram given on p. 555 it is easy to deduce the total light emitted by the sample of compound in a given time, since a surface with a brightness of one equivalent foot-candle emits light at the rate of 0.0011 candle per square inch; the following Table gives the number of candle hours emitted by 1 square inch of luminous compound in powder form:—

Time from manufacture.	Total number of candle hours emitted.
0 ·25 year	0 -09
0.5 ,,	0.14
0.75 ,,	0.18
1.0 "	0 ·20 <sub>5</sub>
1.5 ,,	0 ·25 <sub>5</sub>
Per year subsequently	0.09

Table III.

(2) Suppose the values of k', l and  $B_0'$  to be known for a compound of given radium-content, then for a compound of x times this content, but with the same quality of zinc sulphide, the corresponding values will be xk', l and  $xB_0'$ , for l will be unaffected by the radium-content, being a property of the "active centres" alone. Hence for the first compound  $m = lB_0'/(k'+l)$ , while for the second,  $m' = xlB'_0/(xk'+l)$ .

Now, from Table II on p. 559, it will be seen that samples 1 and 2 contain amounts of radium in the proportion of 32:17. These samples were made up at the same time with the same quality of zinc sulphide. It will be noticed that l is practically the same for both samples, while k' and  $B_0'$  are, to a very close approximation, in the ratio of the radium-contents. Assuming the values given in the Table for the constants of sample 1, the value of m calculated for sample 2 by the formula given above is 69 instead of 68 as observed. In this connection it should be noticed that for samples 4 and 5\* made up at the same time with radium contents in the ratio of 2:1, the observations during the early part of the life showed that the initial brightness was accurately in the same ratio as the radium-contents.

The question of the relation between the characteristic constants and the radium-content of a sample of compound is one of the greatest importance. On the simple theory of exponential decay it is clear that if the rate of decay be assumed proportional to the radium-content (as it is approximately during the early part of the life) a sample of high radium-content will decay at a more rapid rate than one of lower content. Hence the luminosity curves will cross and ultimately the weaker compound will have the greater luminosity. This conclusion, however, is not borne out by experiment, and any conclusion based on it with regard to the most suitable radium-content for long-period use would be fallacious, for experiment has shown that the ultimate luminosities of compounds containing 0.32 and 0.17 mgrm./grm. are practically equal. From an examination of equation 8 on p. 557 it will be

<sup>\*</sup> Paterson, Walsh, and Higgins, loc. cit., p. 237, fig. 11.

seen that a compound tends to an ultimate luminosity value given by  $(k'+l) B_{\infty} - l B_{0}' = 0$ .

Now, as is shown above, if k' and  $B_0'$  be proportional to the radium-content for a given zinc sulphide, we may investigate the relation between  $B_{\infty}$  and the radium-content for any zinc sulphide of known characteristic constants. Assuming k'=5l, and  $B_0'=0.055$  equivalent foot-candle for a compound of content 0.4 mgrm./grm., it is easy to deduce the curve shown in fig. 3, for the relation between the ultimate values of the luminosities and the radium-contents of the samples. From the curve it will be seen that, from the point of view of ultimate luminosity, there is no advantage commensurate with the cost, in using a compound with a greater radium-content than 0.2, or at most 0.3 mgrm./grm.

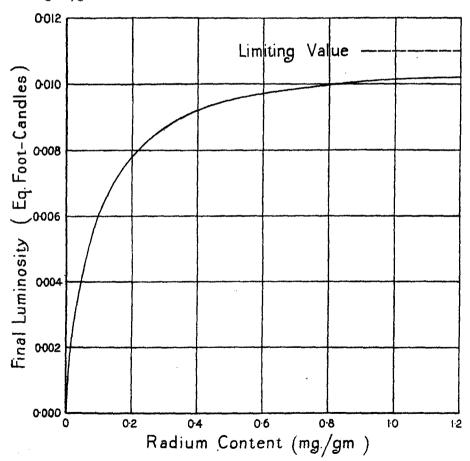


Fig. 3.—Curve showing relationship between radium content and the ultimate value of luminosity.

#### APPENDIX.

#### Mesothorium Compound.

The question of the use of mesothorium preparations in place of radium for luminous compound is of considerable interest and importance from a commercial point of view. The theoretical treatment of the matter is, however, complicated by the fact that (1) mesothorium preparations are sold on a basis of  $\gamma$ -ray activity, and the ratio of this to the  $\alpha$ -ray activity varies throughout the life; (2) there is always considerable contamination with radium; and (3) the mesothorium itself is not  $\alpha$ -active, but its product radiothorium is, so that to predict the behaviour of any compound containing mesothorium it is necessary to know the age of the preparation, *i.e.*, the quantity of radiothorium present.

From the values of the constants of mesotherium and its transformation products, it will be seen that for the present purpose these may, to a near approximation, be grouped under two heads as follows:—

Table IV.

The  $\alpha$ -radiation of radiothorium and its products is, therefore, atom for atom, almost exactly seven times that from radium, or 1.4 times that from radium in equilibrium with its products.

The actual  $\alpha$ -ray activity of a mesothorium preparation at any given period after the time at which it was free from radiothorium is found as follows:—\*

If  $P_0$  be the number of atoms of mesothorium initially present, P the number present after time t, and Q the number of atoms of radiothorium present after time t, then

$$P = P_0 e^{-\lambda_1 t}$$

$$Q = P_0 a \left(e^{-\lambda_1 t} - e^{-\lambda_2 t}\right)$$
where
$$\lambda_1 = 0.126 \text{ (yr.)}^{-1}, \quad \lambda_2 = 0.347 \text{ (yr.)}^{-1}$$
and
$$a = \frac{\lambda_1}{(\lambda_2 - \lambda_1)} = 0.5701.$$

The following Table gives the proportions of mesothorium and radiothorium present during the first 10 years:—

\* Rutherford, loc. cit., p. 421.

(years).	$\mathbf{P}/\mathbf{P}_{o}$ .	$\mathbf{Q/P_{ee}}$	t (years).	$\mathbf{P}/\mathbf{P_0}$ .	$Q/P_0$ .
0	1 '000	0.000	3.6	0.635	0 · 199
0.2	0 975	0 .024	3.8	0.620	0.201
0.4	0 .951	0.046	4.0	0.604	0.202
0.6	0 :927	$0.065^{\circ}$	4.2	0.589	0.203
0.8	0 .804	0.083	4.4	0 .574	0.203
1.0	0.882	0.100	4.6	0 .560	0 204
1 2	0.4860	0.1142	4.8	0 .246	0.203
1.4	888: 0	$0.127^{\circ}$	5.0	0.533	0.208
1 '6	0 .817	$0.138^{\circ}$	5.2	0.519	$0.202^{\circ}$
1.8	0 .797	0 149	5 4	0 '506	$0.200^{\circ}$
2.0	0.777	0.158	5.6	0 1494	0.199
2.2	0.758	0 - 166,	5 '8	0.482	0.198
2 4	0.789	0.173	6.0	0 .470	0 '196,
2.6	0.721.	$0.179_{\mathrm{s}}$	7.0	0.414	0.186
2 '8	0 .703	0.185	8.0	0 .862	0.173
3.0	0.685	0.189	9.0	0.322	$0.158_{6}$
3 · 2	0.668	0 193	10.0	0 284	0.144
3 4	0.651	0.196	1	į	

Table V.

Now considering a sample of mesotherium T years old:

$$\mathbf{Q} = \mathbf{P}_0 a \left[ e^{-\lambda_1(t+\mathbf{T})} - e^{-\lambda_2(t+\mathbf{T})} \right]$$

and equation 7, p. 557, becomes

$$\frac{dn}{dt} = -k'an\left[e^{-\lambda_1(t+T)} - e^{-\lambda_2(t+T)}\right] + l\left(n_0 - n\right),\tag{9}$$

also, and

where

$$B_t \propto na \left[ e^{-\lambda_1 (t+T)} - e^{-\lambda_2 (t+T)} \right]$$
  
 $B_0 \propto n_0 a \left[ e^{-\lambda_1 T} - e^{-\lambda_2 T} \right].$ 

Hence we have

$$f dBt/dt + B_t [k'af^2 + lf^2 - f'] = lB_0 f^2/f_0$$

$$f \equiv e^{-\lambda_1(t+T)} - e^{-\lambda_2(t+T)},$$

$$f'' \equiv -\lambda_1 e^{-\lambda_1(t+T)} + \lambda_2 e^{-\lambda_2(t+T)},$$

$$f_0 \equiv e^{-\lambda_1 T} - e^{-\lambda_2 T}.$$

The solution of this equation is

$$(B_{t}/f) e^{(k'a+l)f_{1}} = (lB_{0}/f_{0}) \int e^{(k'a+l)f_{1}} dt + A,$$

$$f_{1} \equiv -e^{-\lambda_{1}(l+T)}/\lambda_{1} + e^{-\lambda_{2}(l+T)}/\lambda_{2}.$$
(N.B.  $\int f dt = f_{1}, \quad df/dt = f', \quad [f]_{t=0} = f_{0}.$ 

where

The expression under the sign of integration becomes integrable on expansion, so that

$$\frac{B_{t}}{r}e^{(k'a+l)f_{1}} = \frac{lB_{0}}{f_{0}} \left[ t + (k'a+l) \int f_{1}dt + \frac{(k'a+l)^{2}}{2!} \int f_{1}^{2}dt + \dots + \frac{(k'a+l)r}{r!} \int (f_{1})^{r}dt + \dots \right] + A.$$

# 564 The Theory of Decay in Radioactive Luminous Compounds.

The expression on the right, however, is not rapidly converging for the first few terms, so that it is easier to deduce the luminosity curve of a sample of mesothorium paint by successive steps, using the differential equation given above.

This has been done for a number of cases of practical interest and the resulting curves are shown in the diagrams of fig. 4 as follows:—

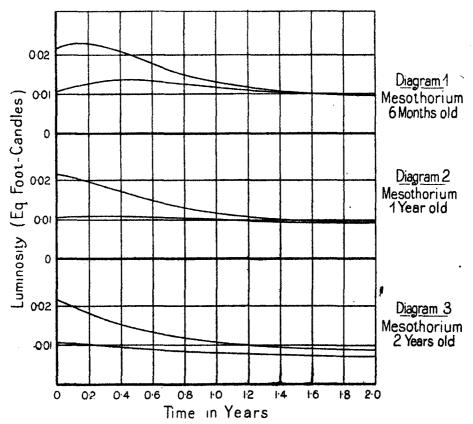


Fig. 4.—Theoretical luminosity curves of various samples of mesotherium compound (see Table VI, p. 565).

Throughout the above calculations, the constants assumed for the zinc sulphide are those found in a typical sample of radium luminous compound. The actual value assigned for k and l is  $0.0016 \, (day)^{-1} = 0.584 \, (year)^{-1}$ . The value of (k'a) in equation 9 given above is found from the relation

$$k'a\left(e^{-\lambda_1 T}-e^{-\lambda_2 T}\right)=k.$$

It will be noticed that the life curves have been calculated on the basis of the initial luminosity only. The actual amount of mesothorium (expressed as equivalent  $\gamma$ -ray activity of radium bromide) is only obtainable from unpublished data relating the  $\alpha$ - and  $\gamma$ -ray activities of radium and mesotherium.

m	al	ما	W	r
	ш	116	v	1.

Age of mesothorium at time of mixing with zinc sulphide.	Initial luminosity of compound at time of mixing.	Life curve on fig. 4.	
1	(= ftcandles.)		
0.5 year	0.0110	1 (lower)	
•	0 .0220	1 (upper)	
1 ·0 year	0 .0110	2 (lower)	
	0 0220	2 (upper)	
2 · 0 years	0.0110	8 (lower)	
• • •	0.0220	S (upper)	

In conclusion, the author would like to express his warmest thanks to Mr. C. C. Paterson for his kind interest and encouragement throughout the work.

On the Reflection of Light from a Regularly Stratified Medium.

By LORD RAYLEIGH, O.M., F.R.S.

(Received June 11, 1917.)

The remarkable coloured reflection from certain crystals of chlorate of potash described by Stokes,\* the colours of old decomposed glass, and probably those of some beetles and butterflies, lend interest to the calculation of reflection from a regular stratification, in which the alternate strata, each uniform and of constant thickness, differ in refractivity. The higher the number of strata, supposed perfectly regular, the nearer is the approach to homogeneity in the light of the favoured wave-lengths. In a crystal of chlorate described by R. W. Wood, the purity observed would require some 700 alternations combined with a very high degree of regularity. A general idea of what is to be expected may be arrived at by considering the case where a single reflection is very feeble, but when the component reflections are more vigorous, or when the number of alternations is very great, a more

<sup>\* &#</sup>x27;Roy. Soc. Proc.,' February, 1885. See also Rayleigh, 'Phil. Mag.,' vol. 24, p. 145 (1887), vol. 26, pp. 241, 256 (1888); 'Scientific Papers,' vol. 3, pp. 1, 190, 204, 264.

detailed examination is required. Such is the aim of the present communication.

The calculation of the aggregate reflection and transmission by a single parallel plate of transparent material has long been known, but it may be convenient to recapitulate it. At each reflection or refraction the amplitude of the incident wave is supposed to be altered by a certain factor. When the light proceeds at A from the surrounding medium to the plate, the factor for reflection will be supposed to be b', and for refraction c'; the corresponding quantities when the progress at B is from the plate to the surrounding medium may be denoted by e', f'. Denoting the incident vibration by unity, we have then for the first component of the reflected wave b', for the second  $c'e'f'e^{-ik\delta}$ , for the third  $c'e'^3f'e^{-2ik\delta}$ , and so on, all reckoned as at the first surface A. Here  $\delta$  denotes the linear retardation of the second reflection as compared with the first, due to the thickness of the plate, and it is given by

$$\delta = 2\,\mu T\cos\alpha',\tag{1}$$

where  $\mu$  is the refractive index, T the thickness, and  $\alpha'$  the angle of refraction within the plate. Also  $k = 2\pi/\lambda$ ,  $\lambda$  being the wave-length. Adding together the various reflections and summing the infinite geometric series, we find

$$b' + \frac{c'c'f'e^{-ik\delta}}{1 - c'^2e^{-ik\delta}}. (2)$$

In like manner for the wave transmitted through the plate we get

$$c'f' + c'f'e'^{2}e^{-ik\delta} + \dots = \frac{c'f'}{1 - e'^{2}e^{-ik\delta}},$$
 (3)

the incident and transmitted waves being reckoned as at A.

The quantities b', c', e', f' are not independent. The simplest way to find the relations between them is to trace the consequences of supposing  $\delta = 0$  in (2) and (3). For it is evident a priori that, with a plate of vanishing thickness, there must be a vanishing reflection and an undisturbed total transmission.\* Accordingly,

$$b' + e' = 0$$
,  $c'f' = 1 - e'^2$ , (4)

the first of which embodies Arago's law of the equality of reflections, as well as the famous "loss of half an undulation." Using these, and substituting  $\eta$  for e', we find for the reflected vibration,

$$\frac{\eta \left(1 - e^{-ikt}\right)}{1 - \eta^2 e^{-ikt}},\tag{5}$$

\* "Wave Theory of Light," 'Ency. Brit.,' vol. 24, 1888; 'Scientific Papers,' vol. 2, p. 64.

and for the transmitted vibration

$$\frac{1-\eta^2}{1-\eta^2e^{-ik\delta}}. (6)$$

In dealing with a single plate, we are usually concerned only with intensities, represented by the squares of the moduli of these expressions. Thus,

Intensity of reflected light = 
$$\eta^2 \frac{(1-\cos k\delta)^2 + \sin^2 k\delta}{(1-\eta^2\cos k\delta)^2 + \eta^4\sin^2 k\delta}$$

$$=\frac{4\eta^2\sin^2(\frac{1}{2}k\delta)}{1-2\eta^2\cos k\delta+\eta^4};\tag{7}$$

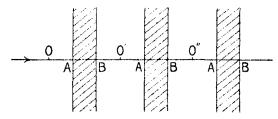
Intensity of transmitted light = 
$$\frac{(1-\eta^2)^2}{1-2\eta^2\cos k\delta + \eta^4},$$
 (8)

the sum of the two expressions being unity, as was to be expected.

According to (7), not only does the reflected light vanish completely when  $\delta = 0$ , but also whenever  $\frac{1}{2}k\delta = s\pi$ , s being an integer; that is, whenever  $\delta = s\lambda$ .

Returning to (5) and (6), we may remark that, in supposing k real, we are postulating a transparent plate. The effect of absorption might be included by allowing k to be complex.

When we pass from a single plate to consider the operation of a number of plates of equal thicknesses and separated by equal intervals, the question of phase assumes importance. It is convenient to refer the vibrations to points such as O, O', bisecting the intervals between the plates; see figure, where for simplicity the incidence is regarded as perpendicular. When



we reckon the incident and reflected waves from O instead of A, we must introduce the additional factor  $e^{-\frac{1}{2}k\delta'}$ ,  $\delta'$  for the interval corresponding to  $\delta$  for the plate. Thus (5) becomes

$$-\frac{\eta (1 - e^{-ik\delta})e^{-\frac{1}{2}ik\delta'}}{1 - \eta^2 e^{-ik\delta}} = r.$$
 (9)

So also if we reckon the transmitted wave at O', instead of A, we must introduce the factor  $e^{-\frac{1}{2}ik(8+\delta')}$ , and (6) becomes

$$\frac{(1-\eta^2)e^{-\frac{1}{2}ik(\delta+\delta)}}{1-\eta^2e^{-ik\delta}}=t. \tag{10}$$

The introduction of the new exponential factors does not interfere with the moduli, so that still

$$|r^2| + |t^2| = 1. (11)$$

Further, we see that

$$\frac{r}{t} = -\frac{\eta (1 - e^{-ik\delta})}{(1 - \eta^2) e^{-\frac{1}{2}ik\delta}} = -\frac{2 i \eta \sin \frac{1}{2} k \delta}{1 - \eta^2},\tag{12}$$

and thus (in the case of transparency) r/t is a pure imaginary. In accordance with (11) and (12) it is permitted to write

$$r = \sin \theta \cdot e^{i\phi}, \qquad t = i \cos \theta \cdot e^{i\phi}, \tag{13}$$

in which  $\theta$  and  $\rho$  are real and

$$\tan \theta = \frac{2 \eta \sin \frac{1}{2} k \delta}{1 - \eta^2}.$$
 (14)

Also from (9), (13)

$$\rho = s\pi - \chi - \frac{1}{2}k(\delta + \delta') - \frac{1}{2}\pi, \qquad (15)$$

where s is an integer and

$$\tan \chi = \frac{\eta^2 \sin k\delta}{1 - \eta^2 \cos k\delta};$$
 (16)

The calculation for a set of equal and equidistant plates may follow the lines of Stokes' work for a pile of plates, where intensities were alone regarded.\* In that case there was no need to refer the vibrations to particular points, but for our purpose we refer the vibrations always to the points O, O', etc., bisecting the intervals between the plates. On this understanding the formal expressions are the same.  $\phi_m$  denotes the reflection from m plates, referred to the point O in front of the plates;  $\psi_m$  the transmission referred to a point  $O^m$  behind the last plate. "Consider a system of m+n plates, and imagine these grouped into two systems of m and n plates respectively. The incident light being represented by unity, the light  $\phi_m$  will be reflected from the first group, and  $\psi_m$  will be transmitted. Of the latter the fraction  $\psi_n$  will be transmitted by the first group, and  $\phi_m$  reflected. Of the latter the fraction  $\psi_m$  will be transmitted by the first group, and  $\phi_m$  reflected, and so on. Hence we get for the light reflected by the whole system,

$$\phi_m + \psi_m^2 \phi_n + \psi_m^2 \phi_m \phi_n^2 + \dots$$

and for the light transmitted

$$\psi_m\psi_n+\psi_m\phi_n\phi_m\psi_n+\psi_m\phi_n^2\phi_m^2\psi_n+\ldots$$

which gives by summing the two geometric series

$$\phi_{m+n} = \phi_m + \frac{\psi_m^2 \phi_n}{1 - \phi_m \phi_n},$$
 (17)

$$\psi_{m+n} = \frac{\psi_m \psi_n}{1 - \phi_m \phi_n}.$$
 (18)

<sup>\* &#</sup>x27;Roy, Soc. Proc.,' 1862; 'Math. and Phys. Papers,' vol. 4, p. 145.

(23)

The argument applies equally in our case, only  $\phi_m$ , etc., now denote complex quantities by which the amplitudes of vibration are multiplied, instead of real positive quantities, less than unity, relating to intensities. By definition  $\phi_1 = r$ ,  $\psi_1 = t$ .

Before proceeding further, we may consider the comparatively simple cases of two or three plates. Putting m = n = 1, we get from (17), (18)

$$\phi_2 = \frac{r(1-r^2+t^2)}{1-r^2}, \qquad \psi_2 = \frac{t^2}{1-r^2}. \tag{19}$$

By (13),  $1-r^2+t^2=1-e^{2i\rho}$ , and thus

$$\phi_2 = \frac{r(1 - e^{2i\varphi})}{1 - r^2}. (20)$$

It appears that  $\phi_2$  vanishes not only when r=0, but also independently of r when  $\cos 2\rho = 1$ . In this case  $\psi_2 = -1$ .

When  $\cos 2\rho = 1$ ,  $r = \pm \sin \theta$ ,  $t = \pm i \cos \theta$ , so that r is real and t is a pure imaginary. From (9) we find that a real r requires that

$$\cos \frac{1}{2}k(\delta + \delta') = \eta^2 \cos \frac{1}{2}k(\delta' - \delta), \tag{21}$$

or, as it may also be written,

$$\tan \frac{1}{2}k\delta \cdot \tan \frac{1}{2}k\delta' = \frac{1-\eta^2}{1+\eta^2}.$$
 (22)

When  $\eta$  is small we see that

$$k(\delta + \delta') = (2s+1)\pi$$
, or  $\delta + \delta' = (2s+1)\lambda/2$ .

In this case only the first and second components of the aggregate reflection are sensible.

If there are three plates we may suppose in (17) m = 2, n = 1.

Thus  $\phi_3 = \phi_2 + \frac{\psi_2^2 r}{1 - \phi_2 r}$ ,

 $\phi_2$  and  $\psi_2$  being given by (19). If  $\phi_3 = 0$ ,

$$\phi_2(1-r\phi_2)+r\psi_2{}^2=0. \tag{24}$$

In terms of  $\rho$  and  $\theta$ 

$$\phi_2 = \frac{\sin \theta (1 - e^{2i\rho}) e^{i\rho}}{1 - \sin^2 \theta e^{2i\rho}}, \qquad \psi_2 = -\frac{\cos^2 \theta e^{2i\rho}}{1 - \sin^2 \theta e^{2i\rho}}.$$
 (25)

Using these in (24), we find that either  $\sin \theta$ , and therefore r, is equal to zero, or else that

$$E^{2}\cos^{4}\theta + E(2-E)(1-E)\cos^{2}\theta + (1-E)^{3} = 0, \qquad (26)$$

**E** being written for  $e^{2i\phi}$ . By solution of the quadratic

$$\cos^2\theta = -(1-E)^2/E$$
 or  $1-E^{-1}$ .

The second alternative is inadmissible, since it makes the denominators zero in (25). The first alternative gives

$$\mathbf{E} = \cos 2\rho + i \sin 2\rho = 1 - \frac{1}{2} \cos^2\theta \pm i \cos \theta \sqrt{(1 - \frac{1}{4} \cos^2\theta)},$$
whence
$$\cos \theta = \pm 2 \sin \rho.$$
(27)

When  $\eta$ , and therefore r, is small,  $\cos \theta = 1$  nearly, and  $\chi$  in (15) may be omitted. Hence

$$\delta + \delta' = \lambda \left( \frac{1}{2} \text{ or } \frac{3}{8} \right) + s\lambda, \tag{28}$$

as might have been expected.

If we suppose  $e^{2i\rho} = 1$ ,  $\phi_2 = 0$ ,  $\psi_3 = -1$ , and (23) gives  $\phi_3 = r$ . It is easy to recognise that for every odd number  $\phi_m = r$ , and for every even number  $\phi_m = 0$ .

In his solution of the functional equations (17), (18),\* Stokes regards  $\phi$  and  $\psi$  as functions of continuous variables m and n, and he obtains it with the aid of a differential equation. The following process seems simpler, and has the advantage of not introducing other than integral values of m and n. If we make m = 1 in (17).

$$\phi_{n+1} = r + \frac{t^2 \phi_n}{1 - r \phi_n},\tag{29}$$

or if we write  $u_n = r\phi_n - 1$ .

$$u_{n+1}u_n + (1 - r^2 - t^2)u_n + t^2 = 0. (30)$$

In this we assume  $u_n = v_{n+1}/v_n$ , so that

$$v_{n+2} + (1 - r^2 + t^2) v_{n+1} + t^2 v_n = 0. (31)$$

The solution of (31) is

$$v_n = \mathbf{H} p^n + \mathbf{K} q^n,$$

where 
$$p+q=r^2-t^2-1$$
,  $pq=t^2$ , (32)

and H, K are arbitrary constants. Accordingly

$$u_n = \frac{Hp^{n+1} + Kq^{n+1}}{Hp^n + Kq^n},$$
 (33)

in which there is but one constant of integration effectively.

This constant may be determined from the case of n = 1, for which  $u_1 = r^2 - 1$ . By means of (32) we get (p+1)H + (q+1)K = 0,

so that 
$$u_n = \frac{(q+1)p^{n+1} - (p+1)q^{n+1}}{(q+1)p^n - (p+1)q^n},$$
 (34)

and 
$$\phi_n = \frac{(p+1)(q+1)\{p^n - q^n\}}{r\{(q+1)p^n - (p+1)q^n\}},$$

\* Stirling has shown ('Roy. Soc. Proc.,' A, vol. 90, p. 237 (1914) that the two equations are not independent, (18) being derivable from (17).

or since by (32)  $r^2 = (p+1)(q+1)$ ,

$$\phi_n = \frac{b^n - b^{-n}}{ab^n - a^{-1}b^{-n}},\tag{35}$$

where

$$\sqrt{\left(\frac{p}{q}\right)} = b, \quad \sqrt{\left(\frac{q+1}{p+1}\right)} = a.$$
 (36)

In order to find  $\psi_m$  we may put n=1 in (17); and by use of (29), with m substituted for n, we get

$$\psi_{m}^{2} = 1 - \phi_{m} \frac{r^{2} + 1 - t^{2}}{r} + \phi_{m}^{2},$$

and on reduction with use of (35), (32),

$$\psi_m = \pm \frac{a - a^{-1}}{ab^m - a^{-1}b^{-m}}. (37)$$

By putting m = 0, we see that the upper sign is to be taken.

The expressions thus obtained are those of Stokes:-

$$\frac{\phi_m}{b^m - b^{-m}} = \frac{\psi_m}{a - a^{-1}} = \frac{1}{ab^m - a^{-1}b^{-m}}.$$
 (38)

The connection between a, b and r, t is established by setting m = 1. Thus

$$\frac{r}{h-h^{-1}} = \frac{t}{a-a^{-1}} = \frac{1}{ah-a^{-1}h^{-1}}.$$
 (39)

In Stokes' problem, where r, t,  $\phi$ ,  $\psi$  represent intensities, a and b are real. If there is no absorption, r+t=1, so that a-1, b-1 are vanishing quantities. In this case

$$\frac{r}{b-1} = \frac{t}{a-1} = \frac{1}{a-1+b-1},$$

$$\frac{\phi_m}{mr} = \frac{\psi_m}{1-r} = \frac{1}{1+(m-1)r}.$$
(40)

and

When m tends to infinity,  $\phi_m$  approaches unity, and  $\psi_m$  approaches zero.

For many purposes, equations (38), (39) may conveniently be written in another form, by making  $b = e^{\beta}$ ,  $a = e^{\alpha}$ . Thus

$$\frac{\phi_m}{\sinh m\beta} = \frac{\psi_m}{\sinh \alpha} = \frac{1}{\sinh (\alpha + m\beta)},\tag{41}$$

$$\frac{r}{\sinh \beta} = \frac{t}{\sinh \alpha} = \frac{1}{\sinh (\alpha + \beta)},\tag{42}$$

where in Stokes' problem  $\alpha$  and  $\beta$  are real, and are uniquely determined in terms of r and t by (44), (46) below.\*

\* Except as to sign, which is a matter of indifference. It may be remarked that his equation (13) can at once be put into this form by making his a and \$\beta\$ pure imaginaries.

If we form the expression for  $(1+r^2-t^2)/2r$  by means of (42), we find that it is equal to  $\cosh \alpha$ . Also

$$\sinh^2\alpha = \frac{\{1 - (r+t)^2\} \{1 - (r-t)^2\}}{4r^2},\tag{43}$$

from which we see that, if r and t are real positive quantities, such that r+t < 1,  $\sinh \alpha$  is real. Similarly,  $\sinh \beta$ ,  $\sinh (\alpha + \beta)$  are real.

Passing now to my proper problem, where r and t are complex factors, represented (when there is no absorption) by (13), we have

$$\cosh \alpha = \frac{1 + r^2 - t^2}{2r} = \frac{\cos \rho}{\sin \theta}, \tag{44}$$

so that cosh a is real. Also

$$\sinh^2 \alpha = \frac{\cos^2 \rho}{\sin^2 \theta} - 1. \tag{45}$$

If we write  $\alpha = \alpha_1 + i\alpha_2$ ,  $\beta = \beta_1 + i\beta_2$ , where  $\alpha_1$ ,  $\alpha_2$ ,  $\beta_1$ ,  $\beta_2$  are real,

 $\sinh \alpha = \sinh \alpha_1 \cos \alpha_2 + i \cosh \alpha_1 \sin \alpha_2$ 

 $\cosh \alpha = \cosh \alpha_1 \cos \alpha_2 + i \sinh \alpha_1 \sin \alpha_2$ 

Since  $\cosh \alpha$  is real, either  $\alpha_1$  or  $\sin \alpha_2$  must vanish. In the first case,  $\sinh \alpha = i \sin \alpha_2$ , and (45) shows that this can occur only when  $\sin^2 \theta > \cos^2 \rho$ . In the second case  $(\sin \alpha_2 = 0)$ ,  $\sinh^2 \alpha = \sinh^2 \alpha_1$ , which requires that  $\sin^2 \theta < \cos^2 \rho$ .

Similarly if we interchange r and t,

$$\cosh \beta = \frac{1+t^2-r^2}{2t} = -\frac{\sin \rho}{\cos \theta},\tag{46}$$

so that cosh  $\beta$  is real, requiring either  $\beta_1 = 0$ , or  $\sin \beta_2 = 0$ . Also

$$\sinh^2 \beta = \frac{\sin^2 \rho}{\cos^2 \theta} - 1. \tag{47}$$

If  $\beta_1 = 0$ ,  $\sinh \beta = i \sin \beta_2$ , which can occur only when  $\sin^2 \rho < \cos^2 \theta$ , or, which is the same,  $\sin^2 \theta < \cos^2 \rho$ . Again, if  $\sin \beta_2 = 0$ ,  $\sinh^2 \beta = \sinh^2 \beta_1$ , occurring when  $\sin^2 \theta > \cos^2 \rho$ .

It thus appears that, of the four cases at first apparently possible,  $\alpha_1 = \beta_1 = 0$ ,  $\sin \alpha_2 = \sin \beta_2 = 0$ , are excluded. There are two remaining alternatives:—

(i) 
$$\sinh^2 \alpha = -$$
;  $\sin^2 \theta > \cos^2 \rho$ ;  $\alpha_1 = 0$ ,  $\sin \beta_2 = 0$ ;

(ii) 
$$\sinh^2\alpha = +$$
;  $\sin^2\theta < \cos^2\rho$ ;  $\beta_1 = 0$ ,  $\sin\alpha_2 = 0$ .

Between these there is an important distinction in respect of what happens when m is increased. For

$$\phi_m = \sinh m\beta / \sinh (\alpha + m\beta).$$

In case (i) this becomes

$$1/\phi_m = \cos \alpha_2 + i \coth m\beta_1 \sin \alpha_2, \tag{48}$$

and  $1/|\phi_m|^2 = 1 + \sin^2 \alpha_2/\sinh^2 m\beta_1,$  (48 bis)

If  $\beta_1$  be finite,  $\sinh^2 m\beta_1$  tends to  $\infty$  when m increases, so that  $|\phi_m|^2$  tends to unity, that is, the reflection tends to become complete. We see also that, whatever m may be,  $\phi_m$  cannot vanish, unless  $\beta_1 = 0$ , when also r = 0.

In case (ii)

$$\pm 1/\phi_m = \cosh \alpha_1 - i \cot m\beta_2 \sinh \alpha_1, \tag{49}$$

and

$$1/|\phi_m|^2 = 1 + \sinh^2 \alpha_1 / \sin^2 m \beta_2, \tag{49 bis}$$

so that  $\phi_m$  continues to fluctuate, however great m may be. Here  $\phi_m$  may vanish, since there is nothing to forbid  $m\beta_2 = s\pi$ . Of this behaviour we have already seen an example, where  $\cos^2 \rho = 1$ .

In order to discriminate the two cases more clearly, we may calculate the value of  $\sinh^2 \alpha$  from (43), writing temporarily for brevity

$$e^{\frac{1}{2}ik\delta} = \Delta, \qquad e^{\frac{1}{2}ik\delta'} = \Delta'.$$
 (50)

Thus by (9) and (10)

$$r = -\frac{\eta (\Delta^2 - 1)}{(\Delta^2 - \eta^2) \Delta'}, \quad t = \frac{(1 - \eta^2) \Delta}{(\Delta^2 - \eta^2) \Delta'},$$
 (51)

so that

$$r \pm t = \frac{1 - \eta \Delta}{(\Delta - \eta) \Delta'}, \quad \text{or} \quad -\frac{1 + \eta \Delta}{(\Delta + \eta) \Delta'};$$
 (52)

whence

$$\sinh^{2}\alpha = \frac{\{(\Delta - \eta)^{2}\Delta'^{2} - (1 - \eta\Delta)^{2}\} \{(\Delta + \eta)^{2}\Delta'^{2} - (1 + \eta\Delta)^{2}\}}{4\eta^{2}\Delta'^{2}(\Delta^{2} - 1)^{2}},$$
 (53)

The two factors in the numerator of the fraction differ only by the sign of  $\eta$ , so that the fraction itself is an even function of  $\eta$ . The first factor may be written

$$\left\{ (\Delta - \eta) \Delta' + 1 - \eta \Delta \right\} \left\{ \Delta - \eta \right\} \Delta' - (1 - \eta \Delta)$$

$$= -\left\{ 1 + \Delta \Delta' - \eta \left( \Delta + \Delta' \right) \right\} \left\{ 1 - \Delta \Delta' + \eta \left( \Delta' - \Delta \right) \right\} ;$$

and similarly the second factor may be written with change of sign of  $\eta$ 

$$-\left\{1+\Delta\Delta'+\eta\left(\Delta+\Delta'\right)\right\}\left\{1-\Delta\Delta'-\eta\left(\Delta'-\Delta\right)\right\}.$$

Accordingly

$$\sinh^{2}\alpha = \frac{\{(1 + \Delta\Delta')^{2} - \eta^{2}(\Delta + \Delta')^{2}\}\{1 - \Delta\Delta')^{2} - \eta^{2}(\Delta - \Delta')^{2}\}}{4\eta^{2}\Delta'^{2}(\Delta^{2} - 1)^{2}}.$$
 (54)

In this, on restoring the values of  $\Delta$ ,  $\Delta'$ ,

$$1 + \Delta \Delta' \pm \eta \left( \Delta + \Delta' \right) = 2e^{\frac{1}{2}ik(\delta + \delta')} \left\{ \cos \frac{1}{2}k(\delta + \delta') \pm \eta \cos \frac{1}{2}k(\delta - \delta') \right\},$$
 and

$$1 - \Delta \Delta' \pm \eta \left( \Delta - \Delta' \right) = -2i \, e^{\frac{1}{2}ik(\delta + \delta')} \left\{ \sin \frac{1}{2}k(\delta + \delta') \mp \eta \sin \frac{1}{2}k(\delta - \delta') \right\}.$$

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$$4\Delta^{\prime 2}(\Delta^2-1)^2=16e^{ik(\delta+\delta')}\cos^2\frac{1}{2}k\delta,$$

and thus

$$\sinh^{2} \alpha = \frac{\left\{\cos^{2} \frac{1}{4} k (\delta + \delta') - \eta^{2} \cos^{2} \frac{1}{4} k (\delta - \delta')\right\}}{\eta^{2} \sin^{2} \frac{1}{2} k \delta} \times \left\{\sin^{2} \frac{1}{4} k (\delta + \delta') - \eta^{2} \sin^{2} \frac{1}{4} k (\delta - \delta')\right\}. \tag{55}$$

The transition between the two cases (of opposite behaviour when  $m = \infty$ ) occurs when  $\sin h \alpha = 0$ . In general, this requires either

$$\eta = \pm \frac{\cos \frac{1}{2} k (\delta + \delta')}{\cos \frac{1}{2} k (\delta - \delta')}, \quad \text{or} \quad \eta = \pm \frac{\sin \frac{1}{2} k (\delta + \delta')}{\sin \frac{1}{2} k (\delta - \delta')}, \quad (56)$$

conditions which are symmetrical with respect to  $\delta$  and  $\delta'$ , as clearly they ought to be.\* In (55), (56),  $\eta^2$  is limited to values less than unity.

Reverting to (43), we see that the evanescence of  $\sinh^2 \alpha$  requires that  $r = \pm 1 \mp t$ , or, if we separate the real and imaginary parts of r and t,  $r = \pm 1 \mp t_1 \mp it_2$ .

If, for example, we take r = -1 - t, we have

$$|r|^2 = (1+t_1)^2 + t_2^2 = 1 + |t|^2 + 2t_1.$$

$$|r|^2 = 1 - |t|^2;$$

$$|r|^2 = 1 + t_1, \qquad |t|^2 = -t_1.$$

Also

so that

1/1 - 1 + 1, | | | | | - |

In like manner by interchange of r and t,

$$|t|^2 = 1 + r_1, |r|^2 = -r_1,$$

showing that in this case  $r_1$ ,  $t_1$  are both negative.

The general equation (55) shows that  $\sinh^2 \alpha$  is negative, when  $\eta^2$  lies between

$$\frac{\cos^2\frac{1}{4}k(\delta+\delta')}{\cos^2\frac{1}{4}k(\delta-\delta')} \quad \text{and} \quad \frac{\sin^2\frac{1}{4}k(\delta+\delta')}{\sin^2\frac{1}{4}k(\delta-\delta')}.$$

This is the case (i) above defined where an increase in m leads to complete reflection. On the other hand,  $\sinh^2 \alpha$  is positive when  $\eta^2$  lies outside the above limits, and then (ii) the reflection (and transmission) remain fluctuating however great m may be. When  $\eta^2$  is small, case (ii) usually obtains, though there are exceptions for specially related values of  $\delta$  and  $\delta'$ .

Particular cases, worthy of notice, occur when  $\delta' \pm \delta = s\lambda$ , where s is an integer. If  $\delta' + \delta = s\lambda$ ,

$$\sinh^2 \alpha = \eta^2 \cos^2 \frac{1}{2} k \delta - 1, \tag{57}$$

and is negative for all admissible values of  $\eta$ , case (i). If  $\delta' - \delta = s\lambda$ ,

$$\sinh^2\alpha = \cos^2\frac{1}{2}k\delta \cdot /\eta^2 - 1, \tag{58}$$

and we have case (i) or case (ii), according as  $\eta^2$  is greater or less than  $\cos^2 \frac{1}{2} k \delta$ .

<sup>\*</sup> That is with reversal of the sign of  $\eta$ , which makes no difference here.

When  $\eta$  is given, as would usually happen in calculations with an optical purpose, it may be convenient to express the limiting values of (56) in another form. We have

$$\frac{1\mp\eta}{1+\eta} = \tan\frac{1}{4}k\delta \cdot \tan\frac{1}{4}k\delta', \qquad \frac{1\mp\eta}{1+\eta} = -\cot\frac{1}{4}k\delta \cdot \tan\frac{1}{4}k\delta'. \tag{59}$$

When the passage is perpendicular, Young's formula, viz.  $\eta = (\mu - 1)/(\mu + 1)$ , gives

$$(1 \mp \eta)/(1 + \eta) = \mu^{\mp 1},\tag{60}$$

µ being the relative refractive index.

We will now consider more in detail some special cases of optical interest. We choose a value of  $\delta$  such as will give the maximum reflection from a single plate. From (5) or (9)

$$\frac{1}{|r|^2} = 1 + \frac{(1 - \eta^2)^2}{2\eta^2 (1 - \cos k\delta)},\tag{61}$$

so that |r| is greatest for a given  $\eta$  when  $\cos k\delta = -1$ . And then

$$r = -\frac{2\eta e^{-\frac{1}{2}ik\delta'}}{1+\eta^2}, \qquad t = \frac{i(1-\eta^2)e^{-\frac{1}{2}ik\delta'}}{1+\eta^2}.$$
 (62)

We may expect the greatest aggregate reflection when the components from the various plates co-operate. This occurs when  $e^{-ik(\delta+\delta')}=1$ , so that in the notation of (50),  $\Delta^2=\Delta'^2=-1$ . The introduction of these values into (54) yields

$$\sinh^2\alpha = -1,\tag{63}$$

coming under (i). The same result may be derived from (57), since here  $\cos \frac{1}{3}k\delta = 0$ . In addition to  $a_1 = 0$ ,  $\sin \beta_2 = 0$ , we now have by (63)  $\sin a_2 = \pm 1$ ,  $\cos a_2 = 0$ , and (48) gives

$$|\phi_m|^2 = \tanh^2 m\beta_1, \qquad |r|^2 = \tanh^2 \beta_1. \tag{64}$$

We are now in a position to calculate the reflection for various values of m, since by (62)

$$\tanh \beta_1 = \pm \frac{2\eta}{1+\eta^2} = \pm \tanh 2\zeta$$

if  $\eta = \tanh \zeta$ , so that

$$\beta_1 = \pm 2 \tanh^{-1} \eta. \tag{65}$$

Let us suppose that, as for glass and air,  $\mu = 1.5$ ,  $\eta = \frac{1}{5}$ , making  $\beta_1 = 0.40546$ . The following were calculated with the aid of the Smithsonian Tables of Hyperbolic Functions. It appears that under these favourable conditions as regards  $\delta$  and  $\delta'$ , the intensity of the reflected light  $|\phi_m|^2$  approaches its limit (unity) when m reaches 4 or 5.

Table I.

m.	mβ₁.	tanh m\$1.	$ \phi m ^2 = \tanh^2 m\beta_1$
1	0 .4055	0 .8846	0 · 1479
2	0.8109	0.6701	0.4490
8	1 .2164	0 .8386	0.7082
4	1 .6218	0 9249	0.8554
5	2 .0273	9659 0	0.9880
6	2 .4328	0.9847	0.9696
7	2 .8382	0.9932	0.9864
10	4 .055	0 .9994	0.9988
œ	oc	1.0000	1.0000

In the case of chlorate of potash crystals with periodic twinning  $\eta$  is very small at moderate incidences. As an example of the sort of thing to be expected, we may take  $\beta_1 = 0.04$ , corresponding to  $\eta = 0.02$ .

Table II.

271.	$\tanh m \boldsymbol{\beta}_1$ .		
1	0.0400	0.00160	
2	0.0798	0.00637	
4	0 · 1586	0.02517	
8	0 -3095	0.09579	
16	0 -5649	0.8191	
32	0 8565	0.7336	
64	0.9881	0.9763	

According to (58), if  $\delta' - \delta = s\lambda$ , the same value of  $\sinh^2 a$  obtains as in (63), since we are supposing  $\cos \frac{1}{2}k\delta = 0$ , and the same consequences follow.\*

Retaining the same values of  $\delta$ , that is those included under  $\delta = (s + \frac{1}{2}) \lambda$  we will now suppose  $\delta' = s' \lambda$ , where s' also is an integer. From (55)

$$\sinh^2 \alpha = \frac{(1-\eta^2)^2}{4n^2} = \sinh^2 \alpha_1,$$
 (66)

since  $\sin \alpha_2 = 0$  in this case (ii). By (49 bis) we have now, setting m = 1,

$$\frac{1}{|r|^2} = 1 + \frac{\sinh^2 \alpha_1}{\sin^2 \beta_2} = \frac{(1+\eta^2)^2}{4\eta^2},$$

as we see from (62). Comparing with (66), we find  $\sin^2 \beta_2 = 1$ ,  $\beta_2 = (s + \frac{1}{2})m$ . Thus  $\sin^2 m\beta_2$  is equal to 1 or 0, according as m is odd or even; and (49 bis) shows that when m is odd

$$|\phi_m|^2 = r^2 = 4\eta^2/(1+\eta^2)^2,$$
 (67)

<sup>\*</sup> But when  $\eta$  is small, a slight departure from  $\cos \frac{1}{2}k\delta = 0$  produces very different effects in the two cases.

and that when m is even,  $|\phi_m|^2 = 0$ . The second plate neutralises the reflection from the first plate, the fourth plate that from the third, and so on. The simplest case under this head is when  $\delta = \frac{1}{2}\lambda$ ,  $\delta' = \lambda$ .

A variation of the latter supposition leads to a verification of the general formulæ worth a moment's notice. We assume, as above,  $\delta' = s'\lambda$ , but leave  $\delta$  open. Since  $e^{\frac{1}{2}ik\delta'} = +1$ , (9) and (10) become

$$r = \mp \frac{e^{\frac{i}{\hbar}ik\delta} - e^{-\frac{i}{\hbar}ik\delta}}{\eta^{-1}e^{\frac{i}{\hbar}ik\delta} - \eta e^{-\frac{i}{\hbar}ik\delta}}, \qquad t = \pm \frac{\eta^{-1} - \eta}{\eta^{-1}e^{\frac{i}{\hbar}ik\delta} - \eta e^{-\frac{i}{\hbar}ik\delta}}; \qquad (68)$$

and these are of the form (39), if we suppose  $a = \eta^{-1}$ ,  $b = e^{\frac{1}{2}ik\delta}$ . The reflection  $\phi_m$  from m plates is derived from r by merely writing  $b^m$  for b, that is,  $e^{\frac{1}{2}imk\delta}$  for  $e^{\frac{1}{2}ik\delta}$ , leaving  $|\phi_m|$  equal to |r|, as should evidently be the case, at least, when  $\delta' = 0$ .

Absorption Bands of Atmospheric Ozone in the Spectra of Sun and Stars.

By A. FOWLER, F.R.S., Professor of Astrophysics, and the Hon. R. J. STRUTT, F.R.S., Professor of Physics, Imperial College, South Kensington.

(Received June 13, 1917.)

#### [PLATE 3.]

#### Introductory.

In a paper communicated to the Royal Society in 1890, Sir William Huggins gave an account of his discovery of a new group of lines in the photographic spectrum of Sirius, situated near the limit of atmospheric transmission.\* A photograph taken with a long exposure was described as showing no strong lines after the termination of the hydrogen series until about  $\lambda$  3338 was reached, at which place there appeared the first of a group of at least six lines, all of which were nearly as broad as those of hydrogen. The third line of the group, about  $\lambda$  3278, appeared to be the broadest. The sixth line occurred almost at the limit of the photograph, where the spectrum was very faint, and it was not possible to determine whether this was the last member of the group. The wave-lengths of the lines, which were only considered to be roughly approximate, were given as 3338, 3311, 3278, 3254, 3226, and 3199.

In 1915, a copy of an excellent photograph of the spectrum of Sirius, \* 'Roy. Soc. Proc.,' vol. 48, p. 216 (1890).

which had been taken with a small quartz prismatic camera at the Royal Observatory, Edinburgh, was kindly forwarded to us by Prof. Sampson. In this photograph the Huggins group is well shown (Plate 3, fig. 3), and it was at once suspected, from the general appearance of the spectrum, that a system of bands, and not a group of lines, was in question. From our knowledge of the physical conditions in the atmosphere of Sirius, as indicated by other parts of the spectrum, the existence of bands in this star seemed highly improbable, and it was an obvious inference that they might be produced by absorption in our terrestrial atmosphere. This view was strongly supported by photographs of the solar spectrum which we obtained with a small quartz spectrograph near sunset, as compared with similar photographs taken when the sun was at a considerable elevation. The spectrum of the low sun showed very decided indications of bands occupying about the same positions as those in the spectrum of Sirius, but, on account of the superposition of solar lines, the wave-lengths of the bands could not be very certainly derived.

The published results of experiments on the absorption of atmospheric gases suggested that ozone was the most probable source of the bands under consideration. Ladenburg and Lehmann\* had, in fact, noted a number of bands in the absorption spectrum of ozone, extending from  $\lambda$  3220 to  $\lambda$  3566, and thus covering a part of the region occupied by the bands observed in Sirius. The wave-lengths given by Ladenburg and Lehmann, however, were not in sufficient agreement with those given by Huggins, or with the provisional wave-lengths communicated to us by Prof. Sampson, to establish the identity of the ozone and Sirian bands. As no other probable origin occurred to us, it was decided to make a new experimental investigation of ozone absorption, and, after some unavoidable delay, the experiments were recently undertaken. The new observations have definitely established that ozone is the origin of the Huggins group of bands in the spectrum of Sirius, and that the same bands are also present in the solar spectrum, with an intensity varying with the sun's altitude.

While this investigation was in progress, our attention was drawn by Prof. Sampson to a dissertation by Otto Kohl,† in which the author gives results of measurements of a number of photographs of ultra-violet stellar spectra which had been taken at Potsdam by Prof. Hartmann in 1904. In this paper, the discovery of the bands near the end of the spectrum was wrongly attributed to Prof. Hartmann, but the additional fact was brought out that they occurred in different stars, irrespective of spectral

<sup>\* &#</sup>x27;Ber. Deutsch. Phys. Gesell.,' vol. 8, p. 125 (1906).

<sup>† &#</sup>x27;Ast. Mitt. König. Sternwarte zu Göttingen,' No. XVI (1913).

types. Thus, the bands were noted in  $\alpha$  Aurigæ,  $\alpha$  Canis Majoris,  $\alpha$  Lyræ,  $\beta$  Orionis, and  $\zeta$  Tauri, as well as in the solar spectrum. There were considerable divergences in the measured positions of the bands, but, in view of their diffuseness and their varying breadths in different spectra, it could reasonably be concluded that they were common to the different stars. The occurrence of the bands in different stars naturally suggested that the whole group had the same origin, and that they might possibly be due to absorption by the earth's atmosphere. There was no evidence, however, for attributing them either to atmospheric oxygen, nitrogen, water-vapour, or carbon dioxide, and there appeared to be no agreement whatever between the stellar bands and the bands of ozone, as recorded by Ladenburg and Lehmann. The alternative supposition that the bands might be of stellar origin likewise received no support from comparisons with metallic spectra, and it was concluded that chemical identification would be necessary to decide whether they were of sidereal or telluric origin.

It should be mentioned that the bands also appear very distinctly in photographs of the spectra of Capella, Vega, and Regulus, taken at Edinburgh on April 12, 1915, and recently forwarded to us by Prof. Sampson.

## Previous Observations of Ozone Absorption.

The general features of the absorption spectrum of ozone have long been known. In the visible spectrum there are several ill-defined bands, which were first described by Chappuis\* in 1880. These bands were also obtained, but less strongly, by Liveing and Dewart in 1889; and, more recently, their positions have been re-determined by Ladenburg and Lehmann. The strongest of these bands, according to Chappuis, extends from  $\lambda$  6095 to  $\lambda$  5935.

A region of strong absorption in the ultra-violet was discovered by Hartley§ in 1880. The central part, where the absorption was most intense, was estimated to be at  $\lambda$  2560, and the band was observed to extend in both directions as the amount of absorbing gas was increased. Hartley concluded, however, that the band would not extend indefinitely with increase in the amount of ozone, and that nearly the maximum effect was produced when all rays with a wave-length less than 2930 were absorbed; that is, it was thought that further additions of ozone would only slightly increase the absorption.

<sup>\* &#</sup>x27;Comptes Rendus,' vol. 91, p. 985, and vol. 94, p. 858.

<sup>† &#</sup>x27;Roy. Soc. Proc.,' vol. 46, p. 222 (1889).

<sup>1</sup> Loc. cit., p. 129.

<sup>§ &#</sup>x27;Jour. Chem. Soc.,' vol. 39, pp. 57 and 111.

Quantitative investigations of the broad ultra-violet absorption band have been made by Fabry and Buisson,\* who used a mercury arc as the source of light, and determined the coefficient of absorption for 10 different wavelengths between 2352 and 3341. The wave-length of maximum absorption was placed at  $\lambda$  2550, in close agreement with Hartley, and ozone was stated to be as opaque for light of this wave-length as are the metals, mass for mass, for visible light.

The ultra-violet bands which form the chief subject of the present communication occur near the less refrangible boundary of the great absorption band. The only previous observations of bands in this region appear to be those of Ladenburg and Lehmann, to which reference has already been made. Burning magnesium was used as the source of light, and it was stated that with small concentration of ozone there was merely a continuous absorption extending to about  $\lambda$  3160, while with a large amount of the gas a number of relatively narrow bands were observed near the limit of absorption towards the red. It was further observed that bands appeared at successively longer wave-lengths as the concentration of ozone was increased. With the greatest concentration obtained by Ladenburg and Lehmann, the complete absorption reached as far as  $\lambda$  3388.

The bands in question probably escaped the notice of Hartley, because the electric spark which he employed as the source of light in his experiments was not well adapted to show them. Fabry and Buisson make no reference to the bands, and it is probable that they also did not observe them on account of the unsuitability of their source of light.

For the sake of completeness, it should be added that the absorption of ozone in the infra-red has been investigated by K. Ångström,† who observed bands which were also found in the solar spectrum.

## Experimental Procedure.

For laboratory observations of the absorption bands a source of light is required which yields a spectrum as continuous as may be, and extending far into the ultra-violet. The absorption bands to be looked for, as will appear later, are very faint over a part of their range, and emission lines or bands, due to the source of light used, add greatly to the difficulty of observing them. After trial of various sources, those selected for use were:

(1) the incandescent crater of the carbon arc; and (2) the light of burning magnesium ribbon, fed by a clockwork lamp. The carbon arc does fairly

<sup>\* &#</sup>x27;Jour. de Phys.,' vol. 3, p. 196 (1913).

<sup>† &#</sup>x27;Arkiv.för Matematik' (Stockholm), vol. 1, pp. 347 and 395 (1904).

well to about  $\lambda$  3000, but beyond this the continuous spectrum thins out, and lines due to impurities have a disturbing effect. Burning magnesium is less convenient for long exposures, but its continuous spectrum has been photographed as far as  $\lambda$  2200, and it shows no lines or bands between that and  $\lambda$  3600, except the strong reversed line at  $\lambda$  2852.

The ozone used was prepared in the ordinary way by means of a Siemens ozoniser. Oxygen from a cylinder was bubbled through sulphuric acid, which gave a rough idea of the rate of flow; then it passed through the ozoniser to the observation vessel, through which a continuous flow was maintained.

The observation vessels were of various kinds. For great thicknesses, glass tubes were used, closed by quartz plates cemented on with sodium silicate. The length of these tubes varied from 8 feet to 18 inches. For small thicknesses, the ozone stream was delivered by displacement into silica flasks or test-tubes placed in front of the slit of the spectroscope.

No strict control was kept over the quantities of ozone in use, but the rate of passage and other conditions in the generator were kept fairly constant, so that the length of the vessel afforded a convenient means of varying the amount of ozone producing absorption.

In other experiments, when the long tube was in use, the tube was first filled with ozone, the ozoniser was then put out of action while the gas stream was left on, so that ozone was slowly displaced by oxygen. During this process, a succession of exposures were made, allowing the spectroscopic changes to be traced.

The greatest concentration of the ozone used was probably less than 1 per cent. Ladenburg and Lehmann were not able to trace any bands when using dilute ozone. They had recourse to the troublesome process of concentrating it by liquefaction. We have not found this to be necessary.

The instrument chiefly employed for the photography of the spectra was a small quartz spectrograph by Hilger, giving a linear dispersion of 58 Å. per millimetre at  $\lambda$  3200. This small dispersion was well adapted for the purpose in view, as most of the bands are rather diffuse, and very precise determinations of their positions are not to be expected. Some of the photographs were taken with copper are comparisons, and the wave-lengths of the ozone bands were determined in the usual manner by the Cornu-Hartmann interpolation formula.

Photographs of the bands were also taken with a much more powerful instrument, giving  $\omega$  dispersion of 7 Å. per millimetre at  $\lambda$  3200, but the bands were so diffuse under these conditions that there was no gain in accuracy as compared with the smaller spectrograph. The latter has also the

advantage of giving spectra comparable in purity and dispersion with those of the instruments employed for the stellar spectra.

The bands were lost altogether when it was attempted to photograph them in the 3rd order of a 10-feet concave grating.

#### The New Observations.

The bands in the visible spectrum have not been considered in this investigation, but as regards the ultra-violet region the new observations are in general agreement with those of previous investigators. Additional features, however, have been noted.

The great absorption band in the ultra-violet is illustrated in fig. 1, Plate 3. These photographs were taken with a cadmium spark as the source of light, and show the broadening of the band which accompanies an increase in the amount of absorbing gas.

In opposition to the statement of Ladenburg and Lehmann, the system of narrow bands was found to be represented even with minute amounts of ozone. They were, in fact, photographed as far as λ 2700 when the layer of dilute ozone was only 1 cm. thick. As the thickness of gas was increased, the more refrangible members of the group were obliterated by the increased extent of the great band, and new members continued to appear just beyond the boundary towards the red. There was, however, a general increase in the distinctness of the bands when the region about  $\lambda$  3100 to  $\lambda$  3300 was reached. The least refrangible band observed was a very faint one at  $\lambda$  3432. It would seem that Ladenburg and Lehmann only measured the spectrum with very large concentration, as they recorded no band more refrangible than  $\lambda$  3220, and their last band towards the red was about \( \lambda \) 3566. The present investigation suggests that the narrow bands continue throughout the whole range of the great absorption band, though they become rather inconspicuous even at λ 2700. The successive appearances of the spectrum with increasing thicknesses of ozone are illustrated in fig. 2, Plate 3. Referring to these spectra, the actual bands seen in (a) do not appear in (b) or (c) because, on account of the general absorption, no light in the region of \$\lambda\$ 2800 can get through. And again, the actual bands seen in (c) do not appear in (a) or (b), because there is not enough ozone to bring them out.

As it was not found possible to obtain the desired range of bands in a single experiment, photographs taken with different concentrations of ozone were used for purposes of measurement, and the results combined. The wave-lengths and intensities of all the bands on the red-side of  $\lambda$  3080 which were sufficiently distinct for measurement are included in Table I. The strongest bands are assigned intensity 10, and the faintest intensity 1.

Bands which appear as pairs or groups are indicated as such by connecting brackets, and those which are of more than average breadth are indicated by the letter "b" following the intensity number.

λ.	Intensity.	λ.	Intensity
8482 · 2	1	∫ <b>3232 ·8</b>	1
3421 4	1	8227 2	10
8402 6	1	8221 .5	10
( 8877 ·7	1	3206 ·8	2
₹ 8874 1	8	₹ 8201 0	88
8865 2	1	8194 -8	6
3846 0	1	8188 8	1
3338 .2	4	3181 .2	1
3881 .2	1 1	∫ <b>8177 ·</b> 0	88
f 3811 ·5	56	18171 ⋅6	4
ີ 8804 1	3	3162 6	26
3284·0	2	1. 8188	8
₹ 3279 ⋅8	86	8187 .4	108
8272 0	3	8114 · 8	88
∫ 8255 ⋅6	5	∫ <b>3</b> 105 ·0	5
8249 .7	8	<b>₹ 3096 5</b>	4
3243 ·0	1 <i>d</i>	8089 · 5	88

Table I.—Wave-lengths of Ozone Absorption Bands.

The wave-lengths of the 12 bands given by Ladenburg and Lehmann, without further description, are 3566, 3503, 346, 3435, 3409, 3376, 3343, 333, 3295, 327, 3235, and 322. The first three are out of range of our observations, and the remainder are not in good agreement with our measures. The band 3295 does not appear in our list, and that at 3235 is only represented by a very faint band at 3232.8. Moreover, the wave-lengths 327 and 322 represent very imperfectly the corresponding groups in our photographs. The strong pairs 3311.5, 3304.1 and 3255.5, 3249.7, which are included in Table I, do not appear at all in Ladenburg and Lehmann's list.

It should be noted that the photographs taken with high dispersion gave no indications of the resolution of the bands into close component lines. A similar result was obtained by Chappuis in the case of the bands which occur in the visible spectrum.

# Ozone Bands in the Spectrum of Sirius.

The Edinburgh photograph of the spectrum of Sirius, of which an enlarged copy is reproduced in fig. 3, Plate 3, is on a scale nearly identical with that employed in the laboratory experiments, the dispersion being 56.5 Å, per millimetre at  $\lambda$  3200. In accordance with the description given by Huggins, there are no strong lines between the end of the hydrogen series and the beginning of

the group of bands which occurs near the limit of the spectrum. Only one distinct line was, in fact, certainly recognised on the photograph in this intermediate region, and by extrapolation from the hydrogen lines this was identified with the iron line 3440.8. This was subsequently used as a standard, in combination with  $H_{\gamma}(\lambda\,4340.7)$  and  $H_{\phi}(\lambda\,3798.0)$ , in the determination of the wave-lengths of the bands. The resulting wave-lengths are included in Table II; where they are compared with the positions assigned by Huggins and by Kohl, the latter being taken as the means of the two wave-lengths stated to represent the edges of each of the bands. The last column of the Table gives the strongest bands of ozone according to our measures.

· Spectrum of Sirius.			Ozone.				
Huggins.	Koh	1.	Fowler & Strutt.				Remarks.
λ.	λ.	Int.	λ.	Int.	λ.	Int.	
3338			8887 -2	2	8888 -5	4	Kohl gives a "line" at 3337.5
3311	_	_	8811 ·9	3b 2	8811 ·5 8804 ·1	5 <i>b</i> <b>3</b>	_
8278	8280 .6	1	3285 ·0 3279 ·8 3272 ·9	2 1 5 1 2 5	8284 0 8279 8 8272 0	3 2 8 <i>b</i> 3	
3254			∫ 8254 ·8 8249 ·7	2	8255 · 5 8249 · 7	5 8	} Kohl gives a "line" at 8249
3226	3 <b>224</b> ·8	2	∫ 8227 ·5 8220 ·0	58 58	8227 ·2 8221 ·5	10 10	
3199	8199 -2	2	8201 ·7 8194 ·8	4	8201 ·0 8194 ·8	83 6	There is possibly a metalli line in Sirius, about 3198.
	<b>3</b> 176 ·6	1	} 3177 ·9 { 8172	5 <i>b</i>	8177 ·0 8171 ·6	88 4	These are only vaguely seperated in Sirius.
	3158 -2	-	3157 3138	9 45 P 46	8156 ·1 8187 ·4	8 10b	Estimates of intensity in ste very uncertain on account of faintness of continuous spectrum.

Table II.—Ultra-violet Bands of Sirius compared with Ozone.

The bands, as a whole, are more diffuse in the photograph of Sirius than in the laboratory spectra, and, making due allowance for the difficulties attending the measurement of band spectra, the agreement in the measured positions of the bands of Sirius with those of ozone may be considered very satisfactory. The proof of the identity of the two sets of bands, however, does not depend so much upon close coincidences in the measured positions of individual bands as upon a general agreement of the wave-lengths and intensities as a whole. This agreement is more convincingly demonstrated by the direct comparison of the spectrum of Sirius with that of ozone, as in fig. 3. A perfect correspondence of the two spectra in the region occupied

by the bands is clearly indicated, there being no strong lines in the spectrum of Sirius to cause complication.

### Ozone Absorption in the Solar Spectrum.

The presence of the Huggins group of bands in the spectrum of the low sun was indicated by numerous small-scale photographs taken during 1915. Measurements of the bands were rendered difficult by the superposition of metallic lines, but the general accordance of wave-lengths was sufficient to prove their identity with the bands appearing in Sirius. Kohl had previously noticed the bands in the sun, as we afterwards learned, but he apparently made no investigation of their varying intensity, and his list included three bands which were not indicated by him as appearing in the spectrum of Sirius.

Conclusive evidence that the bands are of telluric origin is furnished by photographs of the high and low sun, such as are reproduced in fig. 4. These have been selected from a series of 17 negatives obtained between noon and sunset on 1917, May 23, and show the spectrum corresponding to altitudes of the sun 55°, 30°, 10°, 4°, and 1°. It will be observed that as the sun's altitude is reduced there is a general advance of the complete absorption towards the red, accompanied by a gradual strengthening of the bands, so that the appearance of the spectrum about sunset is very different from that near noon. It follows that the bands are produced by absorption in our own atmosphere.

As in the case of Sirius, the identity of the bands with those of ozone is more convincingly demonstrated by direct comparison of the solar and experimental spectra than by attempts to prove exact agreement of wavelengths. The spectrum of ozone given in the lowest strip of fig. 4 was obtained with a concentration closely corresponding to the maximum atmospheric absorption, and it will be seen that ozone accounts completely for the difference between the spectra of the high and low suns in the ultra-violet region.\*

The foregoing investigation gives further substantial support to Hartley's suggestion that atmospheric ozone is the effective agency in fixing the limit towards the ultra-violet to which the solar spectrum can be observed. The extension of the complete absorption towards the red, and the successive appearances of bands of longer wave-lengths, as the sun's altitude becomes lower, correspond precisely with the phenomena observed in the experimental spectra as the quantity of absorbing ozone is increased.

<sup>\*</sup> The apparent lack of exact coincidence about \$3195 is due to an adjacent group of solar lines near the more refrangible edge of the corresponding band of ozone.

It may be that the recognition of these narrow absorption bands of ozone in the ultra-violet spectra of the sun and stars will facilitate investigations relating to atmospheric ozone, as the bands occur in a part of the spectrum which is easily photographed, and only a small spectrograph is necessary to show them.

The authors desire to record their appreciation of the kindness of Prof. Sampson in freely placing at their disposal the Edinburgh photograph of the spectrum of Sirius, which was the origin of the present investigation. They are also indebted to Mr. J. Brooksbank, B.Sc., for a number of photographs of the solar spectrum, and for assistance in preparing the plate for reproduction.

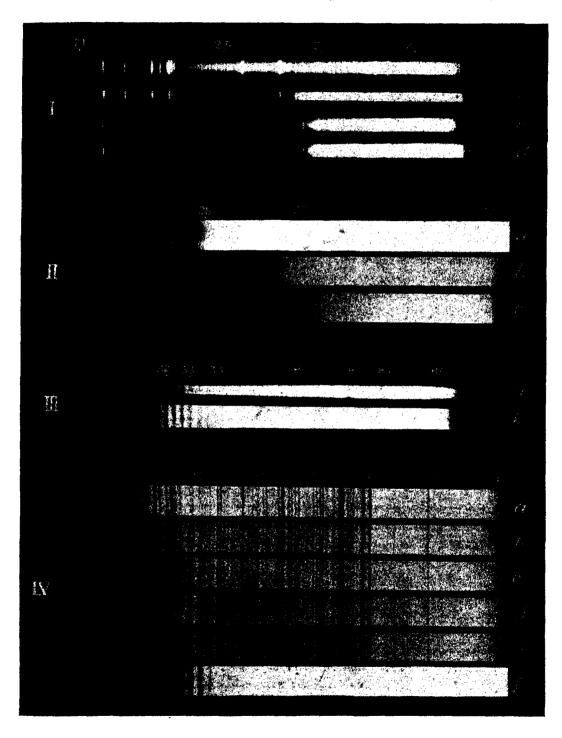
#### DESCRIPTION OF PLATE.

Fig. 1.-To illustrate the great absorption band of ozone in the ultra-violet.

- (a) Cadmium spark, without ozone.
- (b) Absorption due to 1.2 cm. dilute ozone.
- (c) Absorption due to 3.5 cm. dilute ozone.
- (d) Absorption due to 7.5 cm, dilute ozone.
- Fig. 2.—To illustrate the advance of the great absorption band towards the red, and to show the appearance of the narrow bands at successively longer wave-lengths, as the thickness of absorbing ozone is increased. The source of light was burning magnesium, and λ 2852 appears as a reversed line.
  - (a) 1 cm. of dilute ozone, showing faint bands from  $\lambda$  2700 to  $\lambda$  2840.
  - (b) 45 cm. of dilute ozone, showing stronger bands from λ 3000 to λ 3200.
  - (c) 175 cm. of dilute ozone, showing strong bands from  $\lambda$  3150 to  $\lambda$  3432.
- Fig. 3.—The spectrum of Sirius compared with ozone.
  - (a) Spectrum of Sirius, photographed at the Royal Observatory, Edinburgh, on 1915, February 8; altitude of star about 15°.
  - (b) Absorption bands of ozone in the region  $\lambda$  3150 to  $\lambda$  3432.

Fig. 4.—Solar spectra, compared with ozone. Enlarged 5.7 times.

- (a) Sun, altitude 55°
   (b) Sun, altitude 30°
   (c) Sun, altitude 10°
   (d) Sun, altitude 4°
   (e) Sun, altitude 1°
- (f) Ozone absorption bands.





### Note on the Specific Heat of Water. By W. R. Bousfield, M.A., K.C., F.R.S.

(Received June 16, 1917.)

In a paper on the "Specific Heat of Water and the Mechanical Equivalent of the Calorie" were given the figures from 0° to 80° C. which resulted from our investigation. These figures agreed very fairly with those of some other observers,† but differed considerably from the corrected figures of Callendar and Barnes.‡ In our curve there was a minimum value of the specific heat at about 25° C., and a rapid rise afterwards from 25° to 60° of nearly the same magnitude as the fall from 0° to 25°. In the curve of Callendar and Barnes the minimum was not reached till 38° C., and thereafter the rise was much slower.

Callendar soon after devised a novel method of "continuous mixture" by means of an ingeniously devised heat exchanger, and applied this apparatus to test his former results in this range between 60° and 100°. Water at about 100° C, from a heater was passed through the heat exchanger against water from a cooler at from 25° to 35° C. The result of these experiments indicated that the ratio of the mean specific heat from 69° to 100° C, to the mean specific heat from 25° to 56° C, agreed within 1 in 5000 with the ratio derived from Callendar's formula based on the figures of Callendar and and Barnes. These results of this new method were published in Callendar's Bakerian Lecture in 1912,§ and were made the basis of a criticism of our results and those of other observers.

The value of our results in the range which compares with Callendar's new method depends entirely upon the reliability of the correction for evaporation within this range, which is shown graphically in fig. 8 of our paper. A glance at that figure shows that it is not till the temperature of 55° is passed that our correction for evaporation becomes unreliable. We pointed out, with reference to this correction, that:—

"Between 70° and 80° there appears to be considerable uncertainty, especially from 75° to 80° C. This may be partly owing to differences in the amount of air contained in the water, which tends to come off at about this temperature; but it is probably due to some variability in the amount of escape of moisture through the holes in the obturator as the vapour pressure rises."

<sup>\*</sup> W. R. Bousfield and W. Eric Bousfield, 'Phil. Trans.,' A, vol. 211, p. 199 (1911).

<sup>†</sup> See figs. 10 and 11, loc. cit., p. 237.

<sup>‡</sup> See Barnes, 'Roy. Soc. Proc.,' A, vol. 82, p. 390 (1909).

<sup>§ &#</sup>x27;Phil. Trans.,' A, vol. 212, p. 1 (1912).

We have therefore no hesitation in accepting the superior accuracy of the results of Callendar's new method in this region. But Callendar's new figures have only a remote bearing on the values in the lower range and the true position of the minimum. To test the values in the range from 0° to 55° the new method has not been applied, and the difficulties which it was specially designed to meet at higher temperatures hardly exist in the lower range. Over this range the vapour pressure of water is so small that an accurate correction for evaporation can be easily made. The figures which we obtained were closely in line with those of other observers, and the question whether they are more or less correct in this range than those of Callendar and Barnes still appears to be an open one.

According to our corrected figures, the mean specific heat from 13° to 26° is almost exactly equal to that from 26° to 39°, which gives the minimum value in the neighbourhood of 25°. It should not be difficult to apply Callendar's new method to determine this ratio. In the meantime, it is desirable to point out what are the outstanding differences in this lower range, and to refer to some new experiments confirmatory of our former figures. The salient differences in this range of temperature are as follows:—

1. The fundamental figure which was determined by our experiments was the total heat of distilled water, air freed, and having a conductivity of only  $1 \times 10^{-6}$ , between 13° and 55°. The value obtained for the mean specific heat of water from 13° to 55° was

4.182 joules.

The corresponding figure which results from Callendar and Barnes' observations is

4.177 joules.

- 2. The minimum value for the specific heat of water according to our experiments is at 25°, and according to those of Callendar and Barnes at 38°.
  - 3. The specific heat of water at 20° C. deduced from our experiments was

4.176 joules.

That deduced from the experiments of Callendar and Barnes was

4.180 joules.

As to the first point of difference the following observations may be made: The experiments on which our figure was obtained were fairly large scale experiments, there being 3 litres of water in the calorimeter. They were continuous-flow experiments, into which entered no consideration of the capacity of the calorimeter. They were the result of three sets of experiments, each set of experiments having an ascending order of agreement

between individual experiments. Before the last set of experiments the electrical standards and the standard thermometers had all been recently and very carefully re-calibrated at the National Physical Laboratory.

The individual results of the last set of experiments	s were :
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No. of experiment.	Inflow.	Outflow.	Value of J 13 25
161	13 .008	58 982	4 · 1783
162	12 978	54 .88	4 · 1779
164	12 .98	64·14	4 · 1785
165	12 .978	54 16	4 ·1795
166	12 •99	54 · 187	4 ·1785
annual traces - Long-Miller Brooks Management (A1) - 17-7	Mean		4.1785

The mean of these was the value 4.1785 for tap water. The maximum difference between individual values and the mean was less than 1 in 4000.

The range of temperature being 13° to 54°, it was estimated that there might be an error of 0.01 in the temperature readings of any of these 40° intervals. The result shows that the mean error was less. There was no chance of any zero error creeping into the results.

These experiments, each of which involved the use of a large quantity of water, were made on "tap water." The resulting figure was used to determine the capacity of the calorimeter. A series of fifteen subsequent experiments on air-freed distilled water over the same range showed that its mean specific heat was slightly higher, viz., 4·182 from 13° to 55°. Subsequently the total heat of water for each of the three intervals, 13°-27°, 27°-40°, 40°-55°, was determined by four series of experiments, and the sum of the total heats so determined was precisely the same as that directly determined, again giving 4·182 for the mean specific heat from 13° to 55°.

It is suggested that there may be some hidden systematic error in the method. This is, of course, possible, but it seems to be equally possible in the continuous-flow method with platinum thermometry on which the figures of Callendar and Barnes were founded. As a practical unit for calorimetric work the mean specific heat from 13° to 55° still stands pre-eminent, since it can be readily reproduced at all seasons of the year, and easily applied to ascertain accurately the capacity of any calorimeter, a figure which is necessary for nearly all calorimetric work on solutions, where the quantity of solution required forbids the continuous-flow method in most cases.

As to the second point of difference, the position of the minimum, the VOL. XCIII.—A. 3 A

following observations may be made: The course of our curve from 0° to 40° with its minimum at about 25° is in general agreement with the curves of Lüdin, Rowland and Bartoli and Stracciati, whilst the course of the Callendar and Barnes' curve with its minimum at about 38° differs from all.

The results of a paper on the specific heat of certain solutions presented simultaneously with this note confirm our position of the minimum very substantially.\* The old Dewar vessel having been broken it was required to determine the mean capacity of a new and heavier vessel over the intervals 0°-18°, 13°-26°, 26°-39°. A completely different method of regulating the electric current was adopted. In the former experiments the current was kept constant by the use of an ampère balance and simultaneously of a battery of standard cells. In the present experiments the current was regulated so as to keep the energy supply constant by means of a Kelvin watt balance. Moreover, the system of corrections for small heat gains or losses was entirely changed. The capacity was determined by a series of twelve experiments which are set out in the simultaneous communication.

For any interval  $a^{\circ}$  to  $b^{\circ}$ , the total heating of the calorimeter and its contents is given by

$$WS_a^b + C_a^b = 60U / \frac{d\theta}{dt} + \frac{dQ}{d\theta}.$$

where W is the weight of water,  $S_a^b$  the mean specific heat of water for the interval,  $C_a^b$  the mean capacity of the calorimeter for the interval, U the electrical watts,  $d\theta/dt$  the mean rate of rise of temperature per minute and  $dQ/d\theta$  the correction for small heat gains or losses. From these experiments the mean values for the quantity on the right-hand side were determined as

The mean value of W was 3000.1 grm.

The mean values of  $S_a^b$  derived from the former paper, after making a minute correction for the slight variation of capacity of the calorimeter which arises from the expansion of the water from  $0^{\circ}$  to  $39^{\circ}$  were

$$0^{\circ}-13^{\circ}$$
  $13^{\circ}-26^{\circ}$   $26^{\circ}-39^{\circ}$   $S_a^b = 4.193$   $4.175$   $4.175$ 

whilst the corresponding values of Sa from Callendar and Barnes' figures are

$$S_a^b = 4.199 4.189 4.184.$$

<sup>\*</sup> This paper will appear in the 'Philosophical Transactions.'

The respective capacities derived from the first set of figures are

$$C_a^b = 839$$
 857 876

whilst those derived from the second set of figures are

$$C_a^b = 824$$
 815 849.

As the specific heat of glass steadily increases with rise of temperature it is obvious that the second set of capacities is inadmissible. The irregularity of the second set clearly arises from the shifting of the minimum which these figures involve and the regularity of the series of capacities derived from our figures supports the view that the minimum is in the neighbourhood of  $25^{\circ}$ , which gives almost equal values for  $S_{13}^{26}$  and  $S_{26}^{29}$  and not diminishing values.

A further confirmation results from a consideration of the actual values of the specific heats of the KCl and NaCl solutions.

The phenomenon of the minimum value of the specific heat of water undoubtedly arises from the fact that the large proportion of ice-molecules contained in water at the lower temperatures is considerably reduced with rise of temperature, whilst a little later the increasing proportion of steam molecules tends again to increase the specific heat. In saturated solutions of KCl and NaCl the proportion of ice and steam molecules is greatly reduced, and the solvent becomes mainly simple dihydrol. The figures for these solutions indicate a nearly straight line law from 0° to 39° between specific heat and temperature. The fact that the temperature—specific heat curves for saturated solutions of KCl and NaCl come out as nearly straight lines can hardly be a mere coincidence and it entirely depends on getting the right relative values for the capacities for the three intervals.

Until the course of the specific heat curve from 0° to 40° can be considered as definitely settled there must remain a doubt as to the value of the 20° calorie amounting to 1 part per 1,000. The reasons for adopting as the standard calorie the mean specific heat over an interval which undoubtedly includes the minimum point upon either view and which is easily reproducible were stated in the former communication.\* The interval from 13° to 55° satisfies all the practical conditions and there remains a difference of over 1 part per 1000 between our value for the interval and that which results from Callendar's latest figures. It may be hoped that Prof. Callendar may be able to apply his new method to a direct test of the values over this range.

## **OBITUARY NOTICES**

OF

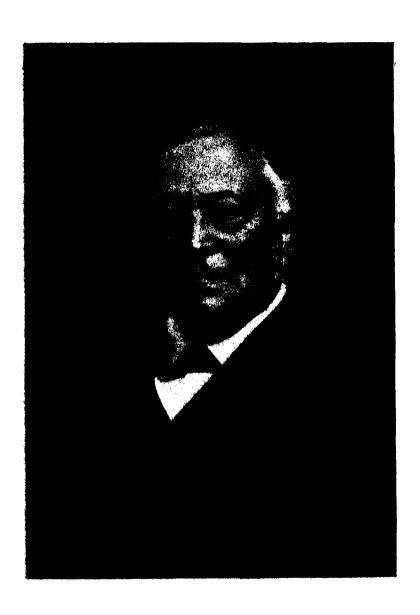
# FELLOWS DECEASED.

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Henry E. Roscoe. Oct 24.

#### SIR HENRY ROSCOE, 1833-1915.

HENRY ENFIELD ROSCOE was born in London on January 7, 1833. His father, Henry Roscoe, was a barrister, who became judge of the Court of Passage, Liverpool. His grandfather was William Roscoe, a banker in Liverpool, and in 1806 Liberal Member of Parliament for that borough. He was a man of remarkable attainments, a generous patron of the Arts, and known in the history of literature as the author of the "Lives" of Lorenzo de Medici and Leo X. Roscoe's mother's maiden name was Maria Fletcher, the daughter of a respected Liverpool merchant, who was chairman of the West Indian Committee. Her maternal grandfather, Dr. William Enfield, author of the well known 'Speaker,' a man distinguished for soundness of literary judgment, was the last Rector of the Warrington Academy, in which Joseph Priestley, the chemist, was a tutor.

Roscoe's father died when he was about four years old. After a few years at a preparatory school, he was sent to the High School of the Liverpool Institute, one of the earliest of the so-called modern schools. Here he came under the influence of Hugo Reid, a well known teacher and writer on natural philosophy, and of W. B. Hodgson, an excellent teacher of English, who afterwards became Professor of Political Economy in the University of Edinburgh. The school possessed a chemical laboratory under the direction of W. H. Balmain, the discoverer of "luminous paint" and of boron nitride, and one of the early contributors to the then newly-founded Chemical Society. He was a stimulating and original teacher, and to him is due the credit of introducing Roscoe to the study of chemistry.

In 1848 Roscoe was entered at University College, London, at that time the only seat of higher learning and research in England open to men who were refused admittance to the older Universities on denominational grounds. Of his teachers at Gower Street, the one who most influenced his career was Thomas Graham. In entering Graham's class-room, Roscoe found himself in a new world, and one indication of the eagerness with which he exploited it may be gleaned from the fact that at the end of his first session he gained the silver medal in chemistry.

Roscoe now elected to follow chemistry as a career. He entered the Birkbeck Laboratory, then under the charge of Williamson, whom Graham had recently brought over from Paris, where he had been working with Laurent and Gerhardt. In his second year Roscoe became Williamson's private assistant, and took part in his researches, and when Graham accepted the Mastership of the Mint, and Williamson succeeded to his chair, Roscoe was made lecture assistant.

It was in recognition of Roscoe's association with Williamson that he was deputed, nearly forty years afterwards, to present, on behalf of the subscribers, the portrait of his master which now hangs in University College.

Having taken his B.A. degree, with honours in chemistry, he decided to enlarge his experience by a course of study in a Continental laboratory, as was then the usual custom. He elected to go to Bunsen, who had recently been called from Breslau to Heidelberg in succession to Leopold Gmelin, the author of the well-known 'Handbuch.' Bunsen had already won for himself a European reputation by his masterly investigation of the cacodyl compounds, by his methods of gas analysis, his studies of the chemistry of the blast-furnace, his invention of the carbon-zinc battery, and of a new type of photometer, and his inquiries into the chemical aspects of the volcanic and pseudo-volcanic phenomena of Iceland.

In the cloisters of the old monastery which then did duty as the Heidelberg laboratory, Roscoe was first indoctrinated into the art and mystery of quantitative chemical analysis, and he there acquired that familiarity with Bunsen's methods and with his system of laboratory instruction that he was to turn to such signal account in the establishment and direction of the Manchester School of Chemistry. One of his earliest quantitative exercises was in silicate analysis, and his first published paper was a joint production with Schönfeld on the composition of certain varieties of gneiss. This appeared in 'Liebig's Annalen' in 1854.

At the close of his second session he passed his doctor's examination summa cum laude, and then embarked on the well-known enquiry, in association with Bunsen, on the measurement of the chemical action of light, which occupied much of his time and energy during the next eight years.

In the obituary notices he wrote for 'Nature' of August 31, 1899, and for the 'Proceedings,' and more especially in the admirable Memorial Lecture he gave to the Chemical Society, Roscoe did ample justice to the memory of Bunsen as a great chemist, pre-eminent as a discoverer and teacher, and lovable as a true and noble-hearted man.

In the autumn of 1856 Roscoe returned to London, and, with the help of friends, set up a private laboratory, with Wilhelm Dittmar to assist him in research work. He also obtained employment as a science lecturer at an army school at Eltham, and did some analytical work on ventilation for a Departmental Committee, the results of which were published by the Chemical Society. The London laboratory was, however, soon given up, for in the following year the late Sir Edward Frankland, the first professor of chemistry in the recently founded Owens College, Manchester, having resigned his appointment, Roscoe offered himself as a candidate for the chair and was elected. The college had been established for about six years in a private house in the vicinity of Deansgate, which had formerly been the residence of Richard Cobden. It had at the time some half-dozen professors and about thirty-five students, fifteen of whom were working in the chemical laboratory which had been fitted up by Frankland.

The college at this period of its existence was at the lowest ebb of its fortunes. It was written down by the local Press as "a mortifying failure," and its financial condition was such that the new professor was refused the

tenancy of a house when the landlord learned that he was one of its staff. In the Manchester of those days there was little appreciation of the bearing of science on an industrial career. The college was the first attempt of the kind to bring the higher training and something of the spirit of collegiate life within the reach of the middle-class youth of a great business community, and it was necessary to have some regard to the special requirements of the district, as well as, it may be, to its prejudices.

Roscoe's antecedents, his associations with Lancashire, and his knowledge of and sympathy with what is best in the Lancashire character, made him quick to realise the conditions upon which the success of the struggling institution must depend. He saw that it was of no use for it to set itself athwart the economic life of the community, and, young as he was-he was twenty-four-he was more alive to the practical necessities of the position than the majority of his colleagues, or indeed of the governing body. It was his immediate aim to establish at Owens College a school of chemistry which should worthily serve the interests of the great manufacturing district of South Lancashire. From the outset he threw himself heartily into the educational and scientific activities of the town in which was to be his home for the next thirty years. He joined the Philosophical Society of Manchester, so honourably associated with the names of Dalton, Joule, and Schunck; for many years he served as its secretary, was a frequent contributor to its publications, and ultimately became its president and an honorary member. He was the first recipient of its Dalton Medal, awarded in recognition of his elucidation of the genesis of Dalton's great theory, based on manuscripts and laboratory note-books in the possession of the Society, and published in association with his pupil and friend, Dr. Harden.\*

The visit of the British Association to Manchester in 1861, when he served as one of the local secretaries, afforded him an opportunity of showing his organising power and business aptitudes. These were still further demonstrated in the winter of 1862, during the memorable cotton famine in Lancashire, when he acted as one of the secretaries to a committee created to provide some form of intellectual occupation for the thousands of operatives thrown out of employment by the stoppage of the staple industry of the district. He gave experimental lectures on subjects likely to attract a working-class audience. These were highly popular, and undoubtedly awakened a general interest in scientific matters. Their success encouraged him to institute the series of Science Lectures for the People which he began in 1866 and carried on for eleven consecutive winters. In this movement he secured the co-operation of Huxley, Carpenter, Tyndall, Huggins, Lord Avebury, Abel, Stanley Jevons, Clifford, Spottiswoode, and others. The lectures were given in some of the largest public halls in the city, and were attended by thousands. They were published week by week as delivered, and were sold for a penny all over the world.

<sup>\* &#</sup>x27;A New View of the Origin of Dalton's Atomic Theory,' by H. E. Roscoe and A. Harden. Macmillan and Co.

Of their stimulating influence Roscoe received abundant testimony; in after life he frequently met persons, some occupying high and responsible positions in commerce and industry, who informed him that they were indebted to these lectures for their first interest in science.

Services such as these, combined with Roscoe's growing popularity and influence in the district, necessarily reacted favourably upon the fortunes of the college, and especially of its chemical department, and the laboratory soon became inadequate to accommodate the students who came to it from all parts of England. The prospects of the college were now so well assured that, in 1867, a town's meeting resolved "that the time had come for the public of the district to unite for the purpose of developing the college on a more comprehensive scale, and in appropriate and convenient buildings." executive committee, on which Roscoe was placed, was appointed to carry out this resolution, and he was called on to serve on certain sub-committees dealing with the new site, buildings, and extension and rearrangement of courses of study. It says much for the influence and power he had now acquired in the councils of the college, and for the confidence reposed in his judgment and business capacity, that he should be called upon to take so prominent and so responsible a share in the extension movement. foundation-stone of the first block of buildings to be erected was laid by the Duke of Devonshire, the first President of Owens College, on September 23, 1870.

The design of the new chemical laboratories was wholly inspired by Roscoe after examining every Continental example that might furnish suggestions concerning internal arrangements and fittings, the details being admirably carried out by the late Mr. Alfred Waterhouse. It is not too much to say of these laboratories that they have served as models for practically every chemical laboratory connected with a collegiate institution that has been subsequently built in this country or abroad.

As the college grew and prospered, and as the scheme of its studies was gradually enlarged until it included nearly every department of learning professed at the older Universities, it was inevitable that sooner or later it should seek for University powers. Many distinguished friends of the college, among them Lord Kelvin and Sir Benjamin Brodie, who had long been interested in its development, were of opinion in the late 'seventies that it had already attained a university position, and that steps should be taken The idea of a university for to make it the University of Manchester. Manchester was as old as 1640, when it was mooted by Henry Fairfax, Rector of Ashton-under-Lyne, and it cropped up again in the latter half of the eighteenth, and also in the early part of the nineteenth century, and it was but natural that it should gradually centre itself around the foundation of John Owens. To Roscoe and his colleagues. Sir A. W. Ward, who was then Professor of History at the college, Principal Greenwood, and Prof. Morgan, belongs the credit of taking the first effective steps towards the realisation of this consummation. "It is to the seal and untiring devotion of these four gentlemen," wrote Mr. Thompson, the historian of Owens College, "that Manchester owes its university; others cordially supported the movement, but they through five weary years placed their case before the public, removed prejudices, advanced good arguments, and lived down opposition."

Opposition, it should be stated, mainly came from Yorkshire, as it had threatened to come in Fairfax's time. The newly-founded Yorkshire College in Leeds considered that its future was jeopardised by the establishment of a university so close to the borders of its own area, and whilst not opposed to the creation of another university in the north of England, prayed that its charter might be so modified as to admit of the inclusion of other institutions of collegiate rank which might be able to fulfil the conditions of incorporation as constituent colleges with a definite share in its government.

This action resulted in the establishment in 1880 of a federal university—the Victoria University—in which Owens College, University College, Liverpool, and the Yorkshire College, Leeds, were the constituent colleges, with its seat in Manchester. The elevation of Mason's College to the dignity of the University of Birmingham was quickly followed by the dissolution of the federal university in Manchester, and each constituent college in time received its own-charter as an independent university.

Some years before Owens College attained to the position of a university, attempts were made to induce Roscoe to sever his connection with it. In 1870 he was offered the Lectureship on Chemistry at St. Bartholomew's Hospital in succession to Dr. Matthiesen, and two years later he was invited to become a candidate for the vacant Chair of Chemistry at Oxford, with the promise of a Fellowship if elected. That he might be Brodie's successor was, he says, a tempting suggestion, but on consideration he felt he had a wider scope and the possibility of greater usefulness in building up the chemical school of Owens College—a decision which he had the satisfaction of knowing met with the warm approval of Huxley and other friends.

Roscoe's method of working his department was wholly modelled on that of Bunsen, as those of his pupils who subsequently repaired to Heidelberg could testify. He gave his lectures at the beginning of the working day, when he retired to his sitting-room to glance through his correspondence whilst the laboratory men were settling to work. He would then go round to each in turn, see what had been done since the previous visit, and give such directions as were necessary. Although the students worked independently and were at different stages of progress, he always knew how each was occupied. With the men engaged on research work or with preparations or on any matter out of the usual routine, he would frequently spend a considerable amount of time.

Although organic chemistry, at his most active period as an investigator, was experiencing an extraordinary development and offering limitless opportunities of discovery, its problems then and, it may be added, at no subsequent time, had more than an academic interest for him. The only

communication dealing with organic chemistry with which his name is associated is a short note on the spontaneous polymerisation of volatile hydrocarbons contributed to the Chemical Society in 1885. The paper had its origin in an observation brought to his notice by a tar distiller, who had observed the formation on standing of a white, crystalline mass, resembling camphor, resulting from the decomposition of phenolic substances at a red heat. The crystalline substance was found to have the molecular formula C<sub>10</sub>H<sub>13</sub>, but its real nature and the mode of its genesis were not made out.

The character of Roscoe's work in original inquiry may also be said to have been entirely moulded by his Heidelberg training, and Bunsen's influence may be traced throughout it. So completely was this the case that, consciously or unconsciously, he seemed never to contemplate attacking any problem that would not have appealed to or have been appreciated by Bunsen. His first research was undoubtedly suggested by Bunsen. As already stated, it resulted in the classical investigation on the laws regulating photochemical action. It was already known that a mixture of equal volumes of chlorine and hydrogen on exposure to light lost its characteristic colour and was converted into hydrogen chloride readily soluble in water. Bunsen conceived the idea of making this reaction the basis of a method of measuring the relative amount of activity of the light-vibrations which are concerned in effecting chemical change. As a matter of fact, the idea was not new, for, unknown to Bunsen, it had already been adopted by Draper, of New York, who had, as he states in his paper in the 'Philosophical Magazine' for December, 1843, "invented an instrument (based upon the same reaction) for measuring the chemical force of the tithonic rays which are found at a maximum in the indigo space, and which from that point gradually fade away to each end of the spectrum." Roscoe's disconsolance on learning that he had been thus anticipated was probably of no long duration. "Do not," wrote Bunsen in reply to the distressing information, "let your discovery of Draper's work disconcert you . . . It appears to me that the value of an investigation is not to be measured by whether something is described in it for the first time, but rather by what means and methods a fact is proved beyond doubt or cavil, and in this respect I think that Draper has left plenty for us to do."

After many fruitless attempts they succeeded in constructing an apparatus in which the defects of Draper's "tithonometer" were obviated, and by which not only accurate comparative determinations could be made, but which enabled them to reduce the chemical action of light to absolute measure. They showed by means of it that the amount of chemical action produced by light from a constant source varied inversely as the square of the distance. They studied more accurately the phenomena of photochemical induction discovered by Draper and the causes which determine its

<sup>\* &</sup>quot;Note on the Spontaneous Polymerisation of Volatile Hydrocarbons at the Ordinary Atmospheric Temperature," by H. E. Roscoe, 'Chem. Soc. Trans.,' vol. 47, p. 669 (1885).

occurrence, and the laws which regulate the chemical action of light after the induction is completed. They proved that the absorption of the chemical rays in passing through a medium varies directly as the intensity of the light, and that the amount transmitted varies proportionally with the density of the absorbing medium. It was found that for a given amount of chemical action effected in the mixture of chlorine and hydrogen an equivalent quantity of light is absorbed, and that the coefficients of extinction of pure chlorine for chemical rays from various sources of light They established a general and absolute standard of are very different. comparison for the chemical action of light, and sought to determine the quantitative relations of the chemical action effected by direct and diffused sunlight, and to investigate the laws which regulate the distribution on the earth's surface of the chemical activity emanating from the sun. also measured the chemical action of the constituent parts of the solar spectrum. The action on the sensitive gaseous mixture showed the existence of several maxima of chemical intensity in the spectrum. The greatest action was observed between the lines G in the indigo and H in the violet, whilst another maximum was found to be near the line I in the ultra-Towards the least refrangible end of the spectrum the action became imperceptible above the line D in the orange, but at the other end of the spectrum the action was found to extend as far as Stokes's line U, or to a distance from the line H greater than the total length of the ordinary visible spectrum.

By investigating the conditions under which it was possible to prepare a photographic paper of uniform and constant sensitiveness, and ascertaining the means by which the darkening of the paper on insolation could be accurately compared with a standard tint, it was found comparatively easy to construct an instrument capable of measuring the chemical action of light effected at any point on the earth's surface by the total sunlight and diffuse daylight in the most widely varying circumstances of climate and atmospheric condition.

This joint research, begun in 1855, occupied its authors until 1862. Roscoe did most of the experimental work, and after his election to the professorship in Owens College in 1857 he spent the greater part of each long vacation in Heidelberg in continuing the inquiry.

The results were communicated to the Royal Society in a series of memoirs, which are published in the 'Philosophical Transactions.' Subsequently he

""Photochemical Researches," by R. W. Bunsen and H. E. Roscoe. Part I. "Measurement of the Chemical Action of Light," 'Phil. Trans.,' 1857, p. 385; Part II. "Phenomena of Photochemical Induction," 'Phil. Trans.,' 1857, p. 381; Part III. "Optical and Chemical Extinction of the Chemical Rays," 'Phil. Trans.,' 1857, p. 601; Part IV. "Comparative and Absolute Measurement of the Chemical Rays; Chemical Action of Diffuse Daylight; Chemical Action of Diffuse Daylight; Chemical Action of the San compared with that of a Terrestrial Source of Light; Chemical Action of the Censtituent Parts of Solar Light," 'Phil. Trans.,' 1869, p. 379; Part IV. "On the Direct Measurement of the Chemical Action of Sunlight," 'Phil. Trans.,' 1863, p. 139.

pursued the subject alone or in association with others. In a short paper, published in 1863, he made a series of measurements of the chemical brightness of various portions of the solar disc by means of standard photographic paper, according to the method described by Bunsen and himself in their last communication,\* and in 1864 he described a method of meteorological registration of the chemical action of total daylight, based on a modification of that originally used by Bunsen and himself. The account of this method was made the Bakerian Lecture of 1865, and is published in the 'Philosophical Transactions' of that year.

In this paper he gives the results of consecutive observations on each day for nearly a month at about midsummer, and compares the chemical action of light at Manchester at the winter and summer solstices and the vernal and autumnal equinoxes. The wide variation in the chemical action of light at different periods of the year was illustrated by the fact that if the integral of that on the shortest day be taken as unity, that upon the equinox will be represented by 7 and that upon the longest day by 25.

In 1866 Mr. Baxendell and he contributed a joint note to the Royal Society on the relative chemical intensities of direct sunlight and diffuse daylight at different altitudes of the sun. They showed from observations made at Manchester and at Heidelberg that the ratio of the chemical intensity of direct to diffuse sunlight for a given altitude at different localities is not constant, but varies with the transparency of the atmosphere, and that this ratio does not in the least correspond with the value of visible intensity as estimated by the eye, the action of the atmosphere being 17.4 times greater on the chemical than on the luminous rays when the sun's altitude is about 25°, and 26.4 times greater when it is 12°.

With a view to the introduction of the instrument into meteorology, and as part of the routine work of an observatory, he caused a regular series of measurements to be made during two years at the Kew Observatory, under the direction of Dr. Balfour Stewart, and in order to gain further knowledge of the variation in the chemical action of light in different areas of the earth's surface he sent the writer of this notice, in 1866, to Para, on the Amazon River, 1° 28' S. of the Equator. The Kew observations showed that the mean chemical intensity at hours equidistant from noon is practically the same on the same day, and that the daily maximum of chemical intensity corresponds to the maximum of solar altitude. Measurements showing the daily rise and fall of chemical intensity for each of the 24 months were obtained, as well as of the biennial variation for the same period. It was pointed out that the curve of yearly chemical intensity is not

<sup>\* &</sup>quot;On the Measurement of the Chemical Brightness of Various Portions of the Sun's Disk," by H. E. Roscoe, 'Roy. Soc. Proc.,' vol. 12, p. 648 (1862).

<sup>+ &</sup>quot;On a Method of Meteorological Registration of the Chemical Action of Total Daylight," by H. E. Roscoe, 'Phil. Trans.,' vol. 155, p. 605 (1865).

<sup>† &</sup>quot;Note on the Relative Chemical Intensities of Direct Sunlight and Diffuse Daylight at Different Altitudes of the Sun," by H. E. Roscoe and T. Baxendell, 'Roy, Soc. Proc.,' vol. 15, p. 20 (1867).

symmetrical about the vernal and autumnal equinoxes. Thus for 100 chemically active rays falling at the spring equinox at Kew there fell at the autumn equinox 167 rays, the sun's mean altitude being the same, the difference being probably due to the greater atmospheric opalescence in the spring.

The Pará observations were interesting from the fact that they were the first measurements of photometric intensity made within the tropics and that they served to dispel certain fallacies about photographic effects in very hot climates at that time current. The observations showed that the relation between the sun's altitude and chemical intensity may be represented by the equation

$$CI_a = CI_0 + const. a$$
,

where  $CI_a$  represents the chemical intensity at a given altitude (a) in circular measure,  $CI_0$  the chemical intensity at the altitude 0, and const. a a number to be calculated from the measurements. Comparisons between the observations at Kew and at Pará on the same days in April showed that the daily mean chemical intensity at the latter place was from 10 to 50 times greater than at Kew, the wide difference being due to the enormous and rapid variations in intensity from hour to hour which the chemically active rays experience in the tropics during the rainy season of the year.\*

The relation between the sun's altitude and the chemical intensity of daylight was more accurately determined by the writer from a long series of observations made by Roscoe's method under a cloudless sky at Moita, near Lisbon, in the autumn of 1867. The fact was confirmed that direct sunlight is robbed of its chemically active rays at altitudes below 10°, and that although the chemical intensity for the same altitude at different places and at different times of the year varies according to the varying transparency of the atmosphere, yet the relation at the same place between altitude and intensity is always represented by a straight line. The differences in the observed actions for equal altitudes, which may amount to more than 100 per cent, at different places, and to nearly as much at the same place at different times of the year, serve as exact measurements of the varying transparency of the atmosphere. As illustrating the wide differences in the daily march of chemical intensity at various places, it was found that when light of unit intensity acting for 24 hours is taken as 1,000, the value of the mean chemical intensity at Kew is represented by the number 94.5, that at Lisbon by 110, and that at Pará by 313.3.†

Roscoe's hope that measurements of the chemical intensity of daylight might become part of the routine work of meteorological observatories has, unfortunately, not been realised. Measurements of the kind undoubtedly

<sup>\* &</sup>quot;On the Chemical Intensity of Total Daylight at Kew and Pars, 1865-1867," by H. E. Roscos, 'Phil. Trans.,' vol. 157, p. 555 (1867).

<sup>† &</sup>quot;On the Relation between the Sun's Altitude and the Chemical Intensity of Total Daylight in a Cloudless Sky," by H. E. Roscoe and T. E. Thorpe, 'Phil. Trans.,' vol. 160, p. 209 (1870).

consume much time, and if properly conducted would require the whole service of a skilled assistant. But considering the enormously important part played by chemically active light in the economy of nature, and more particularly in the phenomena of vegetable life, it cannot be doubted that a sufficiently long-continued series of observations, systematically carried out on a well-considered plan at observatories distributed over the earth's surface, would afford most valuable information concerning the facts of solar energy, and incidentally serve to elucidate many important collateral questions. With the assistance of Mr. Horace Darwin, Roscoe made attempts to devise an automatic arrangement which should minimise the labour of observation, but in the absence of any assurance that such an instrument would be utilised trials with it were discontinued.\*

On leaving Heidelberg to settle once more in London, Roscoe, as already stated, engaged Dittmar as research assistant, and they jointly studied by Bunsen's methods the absorption of hydrochloric acid and ammonia in water, proving that these gases do not obey Dalton and Henry's law.†

He next attacked, first with Dittmar's and then with Schorlemmer's assistance, the nature of aqueous solutions of the common volatile acids of constant boiling point, and showed that although the ratio of acid to water is constant for a definite boiling point under a particular pressure, this does not necessarily indicate the existence of definite hydrates. The composition of the hydrated acid on boiling is wholly dependent on the pressure, a concentrated solution losing acid and a dilute solution losing water until the residue in each case acquires a constant composition, not necessarily in simple molecular proportions, but depending on the pressure under which it is boiled.1

In those days Gmelin's 'Handbuch,' which the Cavendish Society had conveniently translated for us, was the chief repository of chemical knowledge—or the absence of it—and many suggestions as to possible fields of inquiry were to be gleaned from a study of its pages. One such subject was perchloric acid and its compounds, concerning which but little was then known beyond the nature and composition of potassium perchlorate as established by Count Stadion as far back as 1816. Roscoe made a fairly complete study of perchloric acid, its hydrates, and a number of its salts.§

He narrowly escaped serious injury when working with ethyl perchlorate, first prepared, in 1840, by the American chemists Hare and Boye, and known to be extremely unstable. He was engaged in filtering a few cubic centimetres of this liquid when it exploded with great violence, a deep hole

<sup>\* &</sup>quot;On a Self-recording Method of Measuring the Intensity of the Chemical Action of Total Daylight," by H. E. Roscoe, 'Roy. Soc. Proc.,' vol. 22, p. 158 (1874).

<sup>+ &</sup>quot;On the Absorption of Hydrochloric Acid and Ammonia in Water," 'Journ. Chem. Soc.,' vol. 12, p. 128 (1860).

<sup>† &</sup>quot;On the Composition of the Aqueous Acids of Constant Boiling Points," by H. E. Roscoe, 'Journ. Chem. Soc.,' vol. 13, p. 146 (1861); vol. 15, p. 213 (1862).

<sup>§ &</sup>quot;On Perchloric Acid and its Hydrates," by H. E. Roscoe, 'Roy. Soc. Proc.,' vol. 11, p. 493 (1861).

was bored into the base of the wooden filter-stand, and many hundreds of fragments of glass were driven into his hand. That filter-stand was long an object of interest to visitors to the private laboratory of the old Owens College in Quay Street.\*

He also published a short note on thallium perchlorate, which had been prepared by the writer in a pure state, who determined its composition and established its isomorphism with the alkaline perchlorates, the crystallographic characters of which had been already ascertained by Kopp.†

Roscoe's most important contribution to inorganic chemistry was, without question, his well-known research on vanadium and its compounds, which occupied him for the greater part of five years. Some time in 1865 his attention was drawn to the occurrence of small quantities of vanadium in some of the copper-bearing beds of the Lower Keuper Sandstone of the Trias which were then being worked at Alderley Edge and Mottram St. Andrews, in Cheshire. He obtained possession of a large quantity of a lime precipitate, a waste product which was found to contain about 2 per cent. of vanadic acid. It was a most unpromising material, but eventually a method was worked out by which the vanadium was extracted as an ammonium vanadate; this, on heating, yielded an impure vanadic acid. Considerable difficulty was met with in freeing the vanadic acid from accompanying phosphoric acid, which clings to it with great tenacity and modifies its properties. Even small quantities of phosphoric acid cause the vanadic acid after fusion to solidify as a pitch-like amorphous mass quite unlike pure vanadic acid.

It was the writer's privilege to assist in the early stages of this investigation, and it fell to his duty to carry out the various experiments which eventually served to establish the composition of the oxides of vanadium, the true nature of its volatile chloride, the existence of hitherto unknown oxychlorides, and of the mononitride which Berzelius had regarded as the metal, and, lastly, to fix its real atomic weight and to show that it was approximately 16 below that assumed by Berzelius on the mistaken supposition that vanadium compounds were analogous in composition to those of chromium.

It was only very gradually that the true chemical relationships of vanadium revealed themselves. For a time the indications were contradictory and perplexing. The first clue was given by Rammelsberg's observations that vanadinite is isomorphous with pyromorphite and mimetesite—two analogously constituted minerals containing phosphorus and arsenic. The next significant fact discovered was that by the action of a reducing agent it was possible to obtain a solution of a vanadium oxide, which on reoxidation to vanadic acid appeared to require as much oxygen as Berzelius's

<sup>\* &</sup>quot;Note on Perchloric Ether," by H. E. Roscoe, 'Journ. Chem. Soc.,' vol. 15, p. 213 (1862).

<sup>† 4</sup> On the Isomorphism of Thallium Perchlorate with the Potassium and Ammonium Perchlorates," by H. E. Roscoe, 'Journ. Chem. Soc.,' vol. 4, p. 504 (1866).

vanadium, regarded as metal, would have needed. When it was ascertained that the volatile liquid chloride which Berzelius had assumed was a trichloride, and free from oxygen, in reality contained oxygen, and was analogous in composition to phosphoryl chloride, the complication was rapidly cleared up, and the chemical relationships of vanadium to phosphorus, arsenic, and the other members of the trivalent group of the elements were established. This, of course, necessitated revising the formulæ of all vanadium compounds up to that time known. The previsions of Mendeléef's great generalisation would, presumably, have indicated the place of vanadium in the scheme of the chemical elements. When the periodic law was actually promulgated a year or two later, vanadium had already taken up its true position.

Roscoe's first memoir on the subject was read to the Royal Society on December 19, 1867, and was made the Bakerian Lecture of that Session.\*

Part II of "Researches on Vanadium," dealing with the chlorides VCl<sub>4</sub>, VCl<sub>5</sub>, and VCl<sub>5</sub>, and metallic vanadium, which he obtained by heating the dichloride in hydrogen, was presented to the Royal Society on June 16, 1869,† and his last memoir, treating of the bromides and of certain of the metallic vanadates, including vanadinite, which he prepared artificially, on April 7, 1870.‡

With the mention of a short communication "On Two New Vanadium Minerals" (roscoelite and mottramite) to the 'Proceedings of the Royal Society' for 1877,§ and of a lecture on "Recent Discoveries about Vanadium" at the Royal Institution, the above statement includes all Roscoe's published contributions to the chemical history of vanadium. He handed over the further prosecution of the subject to his senior students, and, under his inspiration and direction, a considerable number of communications from the Owens College laboratory were made to the Chemical Society, namely, from Bedson (1876), Crow (1876), H. Baker (1878), Kay (1880), Brierley (1886), Hall (1887), and are published in the 'Transactions.'

Other noteworthy contributions by Roscoe to inorganic chemistry are his study of tungsten compounds, in which he describes the existence of the pentachloride, WCl<sub>5</sub>, and the corresponding pentabromide, WBr<sub>5</sub>, and his discovery of uranium pentachloride, UCl<sub>5</sub>. These compounds are of

<sup>\* &</sup>quot;Besearches on Vanadium. Part 1," by H. E. Roscoe, 'Phil. Trans.,' vol. 158, p. 1 (1868).

<sup>+ &</sup>quot;Researches on Vanadium. Part II," by H. E. Roscoe, 'Phil. Trans.,' vol. 159, p. 679 (1869).

<sup>‡ &</sup>quot;Researches on Vanadium. Part III," by H. E. Roscoe, 'Phil. Trans.,' vol. 160, p. 317 (1870).

<sup>§ &</sup>quot;On Two Vanadium Minerals," by H. E. Roscoe, 'Roy. Soc. Proc.,' vol. 25, p. 109 (1877).

<sup>&</sup>quot;A Study of Certain Tungsten Compounds," by H. E. Roscoe, 'Manchester Lit. Phil. Soc. Proc.,' vol. 11, p. 79 (1872).

T "On a New Chloride of Uranium," by H. E. Roscoe, 'Journ. Chem. Soc., vol. 12, p. 933 (1874).

theoretical interest on account of their "anomalous" character. He also discovered columbium trichloride, CbCl<sub>2</sub>, which he found to have the remarkable property of decomposing carbon dioxide when heated in that gas, with the formation of columbium oxychloride, CbCCl<sub>3</sub>, and carbon monoxide, a type of reaction not exhibited by any other metallic chloride.

He also determined the vapour densities of the chlorides of lead and thallium, which he showed to be normal.\*

An examination of the earth-metals contained in samarskite showed that the new metal announced by Delafontaine under the name of "philippium" was a mixture of yttrium and terbium.† The spark spectrum of terbium was at the same time mapped by him and Schuster. An examination of a specimen of oxide which ought to contain "philippium" in large quantities, should that element exist, showed no conclusive evidence of any other metals than yttrium or terbium.‡

In 1882 he sent a note to the French Academy on a redetermination of the atomic weight of carbon by the method of Dumas and Stas, using Cape diamonds, and obtained the value of 12 002 (O = 16) as the mean of six experiments (A., 1882, 794). He also showed, with the assistance of Schuster, that the spectrum of carbon dioxide furnished by the South African diamond was identical with that furnished by other forms of carbon.

So long as he remained in Manchester Roscoe made occasional contributions to the meetings of the Philosophical Society of Manchester on subjects of general or local interest. Among them were: On arsenic eating in Styria; on a crystallised carbon compound in the Alais meteorite; on the amount of carbonic acid in Manchester air; on the corrosion of leaden hotwater cisterns; Dalton's first table of atomic weights—all of which are printed either in the 'Proceedings' or 'Memoirs' of the Society.

Roscoe was largely instrumental in making spectrum analysis and its initial results generally known in this country. Almost immediately after the publication of Bunsen and Kirchhoff's classical paper in 'Poggendorff's Annalen,' he translated it for the 'Philosophical Magazine.' He also proceeded to give public lectures on the subject, beginning with one at the Royal Institution on March 1, 1861—perhaps the most successful, on account of the novelty and interest of his story, of the many he delivered there.

In 1868 he gave a course of six lectures before the Society of Apothecaries of London. These were afterwards published, with additions, in an admirably illustrated and eminently readable volume. It had a considerable

<sup>\* &</sup>quot;Note on the Specific Gravity of the Vapours of the Chlorides of Thallium and Lead." by H. E. Roscoe, 'Roy. Soc. Proc.,' vol. 27, p. 426 (1878).

<sup>+ &</sup>quot;A Study of some of the Earth-metals contained in Samarskite," by H. E. Roscoe, 'Chem. Soc. Trans.,' vol. 41, p. 277 (1882).

<sup>† &</sup>quot;The Spectrum of Terbium," by H. E. Roscoe and A. Schuster, 'Trans. Chem. Soc.,' vol. 41, p. 283 (1882).

measure of success, a second edition, still more largely augmented being called for within a year. In the preparation of a third and fourth edition he was assisted by his friend, Dr. Schuster. As the successive editions show, the rate at which literature accumulated round the subject was altogether unprecedented in the history of scientific discovery.

Roscoe made an attempt to apply the spectroscope to the Bessemer process of steel manufacture, but he subsequently handed over the study of the peculiarities of the spectrum of the converter flame to his former pupil and assistant, Dr. W. Marshall Watts.

Considering his interest in the subject, comparatively little original work on spectroscopy was published by Roscoe. In addition to the papers mentioned, he was concerned in the following:—

- "On the Effect of Increased Temperature upon the Nature of the Light Emitted by the Vapour of Certain Metals or Metallic Compounds," by H. E. Roscoe and R. B. Clifton ('Manchester Lit. Phil. Soc.,' 1860-62, vol. 2, p. 227).
- "Note on the Absorption-spectra of Potassium and Sodium at Low Temperatures," by H. E. Roscoe and A. Schuster ('Proc. Roy. Soc.,' 1874, vol. 22, p. 362).
- "On the Absorption-spectra of Bromine and Iodine Mono-chloride," by H. E. Roscoe and T. E. Thorpe ('Phil. Trans.,' 1878, vol. 167, p. 207).

Roscoe's services to chemistry are to be measured as much by his contributions to its educational literature as by his efforts to enlarge its boundaries by original inquiry. His various text-books, ranging from 'First Steps' through different grades to the most comprehensive treatise, have proved of the greatest service to the teacher, and have exercised a powerful influence in the diffusion of chemical knowledge in this kingdom and abroad. His 'Lessons in Elementary Chemistry' was first published in 1866, and went through numerous editions, and despite the competition of dozens of similar works is still a favourite class-book. At the suggestion of Lothar Meyer it was translated into German by Schorlemmer and published by Vieweg, and has been largely used in German schools and colleges. Translations have appeared also in Russian, Italian, Hungarian, Polish, Swedish, in modern Greek, Japanese, and in one of the Indian vernaculars.

Still more successful, as regards its sale, was his 'Chemistry Primer,' published in 1870, and intended to serve as the first step in chemistry in schools. It also was translated into Icelandic, Polish, German, Italian, Japanese, Bengali, Turkish, Malayalam, and Tamil.

He also published two text-books on 'Inorganic Chemistry,' one for beginners in conjunction with Dr. Lunt, and a larger one, for more advanced students, in association with Dr. Harden, each of which has reached a second edition.

A far more ambitious undertaking was the large 'Treatise on Chemistry,' in which he had the invaluable co-operation of his colleague Schorlemmer.

The first volume of the work appeared in 1877. Its merits are too well known to need description. The inorganic section has passed through several editions, and has been revised from time to time with the help of many collaborators. The original edition was translated into German by Schorlemmer, and the book has largely replaced the time-honoured Graham-Otto as a text-book in colleges and technical schools. Unfortunately, owing to Schorlemmer's death in 1892, the organic section in the English edition was never finished. It has, however, been completed in the German edition under the direction of the late Prof. Brühl, a circumstance which would seem to throw some light on the comparative position of the study of organic chemistry in this country and in Germany.

Roscoe undertook the editorship of the "Century Series of Biographies of Scientific Men" projected by Cassell and Co., to which he contributed a popular account of the life and work of Dalton—a little book written with much relish and a thorough appreciation of the fine character of its subject.

Some years after he had reached the allotted span he was induced to put together his reminiscences, and his Autobiography appeared in 1906. It is of interest as a record of a singularly full and varied life, and has historical value as the story of the educational changes, particularly in science, which he lived to witness or helped to secure. The book serves also to illustrate many features in its author's own character, and affords a pleasing picture of a singularly happy and successful life—of the life of one whom the Romans would have called "a man of good fortune," that is, of one whose prosperity was not the result of accident or chance, but of wisdom and the capacity to bring its aims and efforts to a successful ending.

Roscoe was elected into the Royal Society in 1863, and served on its Council from 1872 to 1877, and again during two subsequent periods, 1881-83 and 1888-90. He was a Vice-President in 1881-2, and again in 1888-90. As already stated, he gave two of the Bakerian Lectures, and in 1873 was awarded a Royal Medal.

Roscoe was one of the original members of the Society of Chemical Industry, and took a leading part in establishing it on its present basis as a national institution with local sections in many of our principal towns and branches in certain of our Colonies and in America. He presided at the meeting in the rooms of the Chemical Society at which it was constituted, served as its first President, and was the first Chairman of its Manchester Section.

In 1909 he was Honorary President of the Seventh International Congress of Applied Chemistry which met in London in that year. It was his wish that his friend, Dr. Ludwig Mond, as an eminent industrial chemist, should be appointed, but Mond declined the position and proposed Roscoe's name instead at the preceding meeting in Rome.

To Roscoe, therefore, fell the honour of introducing the Prince and Princess of Wales—our present King and Queen—to the meeting of 3000 industrial chemists assembled in the Albert Hall, when the Prince welcomed the

gathering in a felicitous speech. The foreign delegates were afterwards received in private audience by King Edward VII, when Roscoe, as Honorary President, had the honour of presenting them.

Roscoe's first introduction to the British Association was at the Glasgow meeting in 1855, when he acted as Secretary of the Chemical Section. At this meeting he read a paper on the results of a joint investigation with Bunsen on the action of light on chlorine water, afterwards printed in the 'Journal of the Chemical Society.' At the Manchester meeting of 1861, when, as already stated, he acted as one of the local secretaries, he presented a valuable report, jointly with Drs. Schunck and Angus Smith, on the condition of manufacturing chemistry in the South Lancashire district ('Brit. Assoc. Rep.,' 1861, p. 108). At the Bath meeting in 1864 he gave one of the evening lectures on the Chemical Action of Light. At the Liverpool meeting of 1870 he presided over the Chemical Section. Unhappily, at that time, as now, France and Germany were at war. But, alas! neither the cosmopolitan character of science nor more than forty years of that brotherly intercourse among its votaries, which he so confidently hoped would "render impossible the breaking out of disasters so fatal to the progress of science and to the welfare of humanity," as he then witnessed, have served to avert an even more fearful disaster. The small but living fire which he then contended would in the end "surely serve to melt down national animosities" is well-nigh extinguished, and by the action of a nation which claims to be the most enlightened and most cultured of all nations.

In 1884 he again served as President of the Chemical Section at the meeting in Montreal. In 1887 he was President of the Association at the Manchester meeting in that year—an honour he prized all the more on account of his long association with that city. The meeting was notable as being the largest held since the foundation of the Association, and was remarkable for the number of foreign chemists present.

Roscoe continued to direct the Chemical Department of Owens College until his election as Member of Parliament for the Southern Division of Manchester in the autumn of 1885.

From the outset he was firmly convinced that the great blot in English industrial life was a singular want of appreciation of one of the essential conditions of success, namely, a sound training in the scientific principles which underlie all practice. That the practical result of working the Owens College chemical department in full recognition of this fact was satisfactory was proved by the steady increase in the number of his pupils, session after session, and the variety of responsible positions many of those pupils subsequently filled. When he laid down his office he could point to the fact that his laboratories, spacious as they were then thought to be, had been more than full during the previous half-dozen years. It has been calculated that upwards of 2000 men had passed through them. No similar place in the kingdom could show such a record of contributions to chemical knowledge. From first to last it had furnished 235 original

communications, mainly to the 'Journal of the Chemical Society' and the 'Proceedings' and 'Transactions' of the Royal Society.

During the tenure of the Professorship of Chemistry at Owens College, Roscoe was called on to serve on two important Royal Commissions. The first was that on Noxious Vapours, which led to the amendment and extension of the Alkali Acts of 1891 and 1892. The second was the Commission on Technical Instruction in 1881—one of the most important and valuable Commissions ever issued when regard is had to its influence on the industrial welfare of this country. Roscoe threw himself heart and soul into its work, for he was profoundly convinced of its importance. During the ten years that succeeded the publication of its report he, in common with several of his colleagues, addressed innumerable public meetings in order to make its lessons known as widely as possible. All this labour bore fruit in the Technical Instruction Act of 1889, and still later, and to a fuller extent, in the Education Act of 1902—a measure preceded by Lord Bryce's Commission on Secondary Education, of which Roscoe was a member.

In spite of what had been accomplished, he was far from being satisfied with our national position. As late as 1906 he wrote:—"Much remains for us in England to accomplish in the organisation of our secondary and scientific training, in which our competitors are before us, and of which the importance and the effects are well summed up in the following opinion of an eminent German manufacturer: 'We in Germany do not care whether you in England are Free Traders or Protectionists, but what we are afraid of is that some day your people will wake up to the necessity of having a complete system of technical and scientific education, and then with your energetic population, with your insular position, and with your stores of raw material, it will be difficult, or it may be impossible, for us to compete.'"

In 1884 a Knighthood was conferred on him, "in acknowledgment of his distinguished service on the Technical Education Commission."

Roscoe was long and honourably connected with the University of London. A graduate in 1853, he acted as an examiner in chemistry from 1874 to 1878. It was largely through his action that laboratory work was introduced into the curriculum in chemistry for science degrees. This not only greatly enhanced their value, but reacted beneficially on the general character of laboratory instruction throughout the country. On relinquishing Parliamentary work he became a member of the Senate, and in 1896 succeeded Sir Julian Goldsmid as Vice-Chancellor. It was during his term of office that the Act of 1898, which reconstituted the University, was passed. He had as Vice-President of the Association for Promoting a Professorial (Teaching) University for London, of which Huxley was President, made proposals with the idea of uniting what have come to be called the internal and external functions of the University, and in his evidence before Lord Cowper's Commission which preceded the Act of 1898 he suggested machinery of a less cumbrous and, as he hoped, of a more satisfactory character than that which became law. As Vice-Chancellor it became his duty to watch the progress of the measure, and to use his influence in promoting its passage, and his Autobiography reveals how actively he exerted himself to this end. The Statutory Commission which followed the University of London Act of 1898, reported in 1900, its provisions were approved by Parliament in June of that year, and the new Senate held its first meeting in the following October. Roscoe took an active share in the re-arrangements consequent on the reconstitution of the University, and in the changes necessitated by its removal from Burlington Gardens to the buildings of the Imperial Institute at South Kensington. Not the least of the services he thus rendered was his action with regard to the election of Sir Arthur Rücker as its first Principal. It was largely through his efforts that the appointment was made. Its success more than justified those efforts, and he always spoke of it as the best day's work he ever did for the University.

Roscoe resigned the Vice-Chancellorship in 1902, when he presented to the University the handsome mace which now lies on the table during the meetings of the Senate, and is used on ceremonial occasions. It was so employed, draped in crape, at the memorial service in Rosslyn Hill Chapel at his death. He remained a member of the Senate until 1910, when age and increasing deafness necessitated his retirement.

Roscoe was a Fellow of Eton College, as a representative of the Royal Society, from 1889 to 1912, and did what he could during the twenty-three years he served on the Governing Body to overcome what he terms " the enormous inertia of this aucient machine." He sought to further the teaching of physical science in the school by himself giving lectures, and through his efforts it is the richer by no less than one large and one small physical laboratory, a physics lecture-room, a workshop, and two more chemical laboratories, with store-rooms, etc. He also reorganised the system of teaching, and introduced graduated courses, which have resulted in an all-round improvement. Nevertheless, the results have not been commensurate with all the hard work and enthusiasm he put into his efforts. They have been largely discounted by factors over which he had no control. No one realised this more clearly than himself, and he felt keenly the disappointment of his hopes, so much so that more than once he considered the advisability of resigning his Fellowship as a protest. He earned the gratitude of the science staff by his uniform kindness and sympathy and by the readiness with which he would discuss their difficulties with them and help them with advice and encouragement.

As the representative of the Royal Society his chief interests lay with the teaching of physical science, but they did not rest there. No Fellow worked harder for the general welfare of the school. In order to make himself acquainted first-hand with facts connected with the subjects to be discussed at the meetings of the Provost and Fellows, he constantly visited Eton. His opinion and advice on all sorts of questions were sought and respected, and he has left behind him a record of whole-hearted

service to the school that will long be remembered with appreciation and gratitude.

His wide experience as an educationist, and in particular his success in furthering the development of Owens College, naturally caused him to be consulted when institutions of a similar type were projected, and he was occasionally induced to take part in their government. Thus he had a large share in the arrangement of the curriculum of University College, Dundee, in 1881, and he was afterwards concerned, as a member of the Scottish Universities Commission, in establishing the connection of that College with the University of St. Andrews. He was appointed by the Duke of Devonshire to a governorship of University College, Liverpool, a position particularly gratifying to him as a member of a distinguished Liverpool family. He had a seat on the Council of Firth College, Sheffield, as a representative of the University of London, and was of service with respect to its science curriculum.

In 1888 he acted as a member of an Executive Commission appointed to carry out the provisions of the Scottish Universities Act. The Commission succeeded in devising ordinances which in many respects revolutionised the systems of the Scottish universities by providing new avenues to degrees, and thus, it may be hoped, affecting to an important extent the character of scientific education in Scotland.

In 1889 he was appointed a member of a Committee to act with the Commissioners of the 1851 Exhibition in drawing up a scheme for the establishment of research scholarships, and in 1896 he succeeded Lord Playfair as Chairman of the Scholarships Committee, and became a member of the Board of Management.

In 1901 he consented, on the invitation of Lord Elgin, the Chairman, to join the Executive Committee of the Trustees appointed to administer Mr. Carnegie's munificent gift to the Scottish universities for the benefit of scientific education, and he assisted in the inauguration of a system of Carnegie scholarships and fellowships for the encouragement of original investigation resembling that of the Royal Commissioners of the 1851 Exhibition.

Roscoe's high appreciation of Pasteur's early work as a chemist was, we may presume, the immediate cause of the interest with which he had followed his remarkable discoveries concerning the causes and cure of chicken cholera, anthrax, and the silkworm disease—an interest quickened, no doubt, by the circumstance that he had made his personal acquaintance as far back as the early 'sixties. He had informed himself of the working of the Institut Pasteur in Paris, and with the details of the anti-rabic treatment, and had borne his share in combating the mischievous prejudices of those in this country who had sought to misrepresent the character and objects of Pasteur's work. In 1886 he had used his Parliamentary influence to induce Mr. Chamberlain, then President of the Local Government Board, to appoint a Government Commission consisting of Lord Lister, Sir James Paget,

Professor Ray Lankester, and himself, with Sir Victor Horsley as secretary, to enquire and report on the efficacy of Pasteur's treatment of hydrophobia. They came to the conclusion, based on irrefragible proof, that this system had saved a large number of lives that otherwise would have been sacrificed to a dreadful death. This report induced Sir James Whitehead, when Lord Mayor of London, to call a Mansion House meeting for the purpose of raising a fund with the double object of offering some acknowledgment of our indebtedness to Pasteur and his institute for having gratuitously treated some 200 of our countrymen, and of defraying the cost of sending poor persons who may need treatment to Paris. The Royal Society requested Roscoe with Sir James Paget and Prof. Lankester to represent them at the meeting, and supported its object by a formal letter from the President. Roscoe, having occasion to respond for "Science" at a Royal Academy banquet, seized the opportunity again to direct attention to the subject, and he afterwards spoke in the House of Commons of the great value of experiments on living animals in opposition to an amendment designed to impede the working of the Vivisection Acts. By memorials, popular lectures, and articles in the periodical Press, he kept the subject continually before the public eye. Nor were his colleagues less active in instructing and forming public opinion. Their efforts eventually resulted in the establishment of an institute in London with aims similar to those of that in Paris. Thanks to the munificent generosity of Lord Iveagh, it has been housed and equipped not less worthily than its sister foundation in France. The London Institute of Preventive Medicine now bears the honoured name of Lord Lister, its first President. Roscoe was the first chairman of its governing body, and up to the last continued to take a keen and active interest in its beneficent work.

Roscoe's services to science and the cause of education were recognised all the world over. He was D.C.L. of Oxford and LL.D. of Cambridge, Dublin, Glasgow, and Montreal; D.Sc. of Aberdeen, Liverpool, and Victoria. On the occasion of the eighth jubilee of the foundation of Heidelberg University, he was made an honorary M.D. He was an Officer of the Legion of Honour, and a corresponding member of the French Institute of the Academy of Sciences. He was an honorary member of the American Philosophical Society of Philadelphia, of the New York Academy of Sciences, of the Chemical Society of Berlin, the Bunsen Gesellschaft, the Verein für Naturwissenschaft of Brunswick, the Physikalische Verein of Frankfort; a corresponding member of the Bavarian Academy of Sciences of Munich, and of the Royal Society of Sciences of Göttingen, the Reale Accademia dei Lincei, Rome, the Academy of Natural Sciences of Catania, Leop. Carol. Akad. of Halle, and of the Physiogr. Sällsk. of Lund. He was an honorary member of the Royal Irish Academy, and of the Literary and Philosophical Society of Manchester. In 1912 the Franklin Institute awarded him the Elliott Cresson Medal.

He was sworn of the Privy Council in 1909—an honour which he

regarded less as a personal distinction than as a recognition of the claims of science.

In 1863 he married the lady whom he had first met, some 10 years previously, in the house of his uncle, Mr. Justice Crompton-Lucy, the youngest daughter of Mr. Edmund Potter, M.P. for Carlisle, a well-known Manchester merchant, and a friend and co-worker of Cobden and Bright. She died in 1910. Of this union all that can be said here is: "Of the 47 years of married life, one who looked on can say there never were two more of one heart and mind." The one great sorrow of their lives was the death of their only son when an undergraduate at Oxford just when he was entering on manhood. He was a youth of much promise and of great charm of manner, and had already given evidence of considerable literary ability. Two daughters were also born of this marriage, the elder of whom is married to Mr. Charles Mallet, formerly M.P. for Plymouth and Under-Secretary for War in the late Liberal Government.

Time dealt tenderly with Roscoe. His vigorous, manly frame and healthy constitution seemed to defy the ravages of age. Except for increasing deafness and recurrent attacks of gout—a dispensation which he used ruefully to observe he had done nothing to deserve—his burden of years sat lightly on him. His happy temperament, no doubt, contributed to this alleviation. A singularly calm and equable disposition, habitual cheerfulness, a constant tendency to see and believe the best of things and of people, strong social instincts, a saving grace of humour, and a generous, impulsive hospitality—these characteristics through life were as strongly marked in him at fourscore years as at 40. On the evening of his death he was forming plans to celebrate his approaching birthday in the society of a chosen few of his old pupils. His mental activity never seemed to diminish. During the last years of his life much of it was exercised in efforts to avert, so far as in him lay, a catastrophe which he felt to be impending, and which, when it came, cast a shadow over the few months that were left to him.

He died at his Surrey home on the morning of December 18, 1915. His end came wholly unexpectedly, swiftly, and almost painlessly; it was just such a passing as he would himself have wished. Happy through life, he was happy also in the manner of his death.

T. E. T.

#### H. G. J. MOSELEY, 1887-1915.

HENRY GWYN JEFFREYS MOSELEY was born on November 23, 1887. He was the son of the late Prof. H. N. Moseley, F.R.S., Linacre Professor in the University of Oxford, and of Amabel, daughter of the late John Gwyn Jeffreys, of Ware Priory, Herts. On both sides he was descended from families who had shown unusual scientific abilities. His father, an investigator of unusual powers, was the son of Canon Moseley, F.R.S., a distinguished mathematical physicist, while his maternal grandfather, Mr. Gwyn Jeffreys, was a Fellow of the Royal Society, and a well known authority on zoology. Prof. Moseley died soon after his son's birth, and the upbringing and education of Moseley was left entirely in the hands of his mother.

Moseley entered Eton at the age of thirteen with a King's Scholarship, and distinguished himself both in classics and mathematics. At the age of eighteen he entered Trinity College, Oxford, with a Millard Scholarship in Natural Science. He obtained his degree with Honours in Natural Science in 1910.

Moseley early showed marked originality and an enthusiastic interest in science. A year before his graduation he decided to undertake original work in physics, and visited Manchester to discuss with the writer the prospects of starting an investigation in radioactivity. After graduation he was appointed Lecturer and Demonstrator in the Physics Department of the University of Manchester, and devoted all his spare time to original investigation. In order to obtain more time for his researches, he resigned his lectureship after two years, and was awarded the John Harling Fellowship. He later returned to Oxford to live with his mother, and to continue his experiments in the laboratory of Prof. Townsend.

In the summer of 1914 he travelled with his mother, via Canada and the Pacific, to take part in the meetings of the British Association in Australia. He took a prominent part in the discussion at Melbourne on the Structure of the Atom, and at Sydney gave an interesting account of the bearing of his researches on X-ray spectra on the number of elements present in the rare-earth group. War had been declared on his arrival in Australia, and as soon as his duties to the Association were completed, he gave up all thought of continuing his scientific investigations, and returned to England to offer his services to his country. He was granted a commission in the Royal Engineers, and later was made signalling officer in the 38th Brigade of the First Army, leaving for the Dardanelles on June 13. He took part in the severe fighting at the Suvla Bay landing on August 6 and 8, and was instantaneously killed on the tenth, by a bullet in the head, when in the act of telephoning an order to his division, at the moment when the Turks were

\* This and other obituary notices of distinguished men of science, not Fellows of the Society, who have fallen in the War, appear in pursuance of a resolution of Council.

· attacking on the flank only 200 yards away. One of his fellow officers, who was present with him, sends the following appreciation:—

"Let it suffice to say that your son died the death of a hero, sticking to his post to the last. He was shot clean through the head, and death must have been instantaneous. In him the brigade has lost a remarkably capable signalling officer and a good friend; to him his work always came first, and he never let the smallest detail pass unnoticed."

Moseley's first research was specially chosen to give him experience in accurate measurement and in methods of obtaining high vacua. The appearance of a large number of groups of \(\beta\)-rays of definite velocities of radium B and radium C made it important to settle definitely how many \(\beta\)-particles were expelled on an average from each disintegrating atom of radium B and radium C. For this purpose, it was necessary to measure the charge carried by the B-rays in a high vacuum, and to disentangle the effects of the two products. Moseley was able to show definitely that on an average one B-particle was emitted during the transformation of one atom of radium B or of radium C. The results of this research, which involved a large amount of careful and accurate experimental work, were published by the Royal Society. Moseley next proceeded to examine whether there was any limit to the positive potential which an insulated body containing radium would reach in a high vacuum. It had long been known that a tube containing radium in a vacuum gained a positive charge due to the escape of swift electrons. property is well illustrated by the little apparatus called a radium clock. The most suitable methods for obtaining and holding the highest possible vacua were studied. Ingenious devices were used for measuring, in situ, the potential reached by a silvered quartz sphere, insulated in the vacuum chamber, containing a large quantity of radium emanation. He was able in this way to obtain a rise of potential of over 100,000 volts, and to retain it for several weeks as the emanation decayed. It was hoped at first that this method might be employed to throw light on the distribution of velocities of the \$\beta\$-rays; but this was found to be impracticable under experimental conditions.

In the meantime, Moseley had devised a simple but powerful method for measuring the rate of decay of products which had much too short a life to detect by ordinary methods. For this purpose, the active matter of short life was deposited on a rapidly rotating disc, and its activity measured at short angular intervals. During this investigation, in which he was assisted by Dr. Fajans, Geiger opportunely discovered the existence of a short-lived product both in the thorium and actinium emanations. Moseley and Fajans applied the method to determine the average life of these products, and showed that the average life of the product actinium A was only 1/300 of a second. Other minor investigations were also undertaken, one with Dr. Makower, on the emission of  $\beta$ -rays from radium B, and another with

Mr. H. Robinson, for the accurate determination of the total ionisation produced by the  $\gamma$ -rays from radium.

Moseley was much interested in the discovery by Laue of the diffraction effects produced by the passage of X-rays through crystals. In conjunction with Mr. C. G. Darwin an investigation was immediately started to make a systematic examination of the amount of scattering of X-rays falling at various angles on different crystals. It was thought likely that the scattering effects would be very small, and some time was spent in developing a very sensitive. electrical detector depending upon the principle of ionisation by collision in a small vessel containing pure helium. While these experiments were in progress, Prof. Bragg, who had commenced a similar investigation at Leeds, informed them that he had found evidence of definite maxima in the scattered radiation, indicating the presence of bright lines in the X-ray spectra. Moseley and Darwin were able to confirm this important point immediately? and mapped out for the first time the bright lines in spectra given by the "L" radiation from a platinum anticathode. These experiments, in the Universities of Leeds and Manchester, were of a fundamental character, and laid the foundation of the now rapidly developing science of X-ray spectroscopy. This new science has already had most important consequences in two main directions. In the hands of Prof. Bragg and his son, the diffraction of X-rays by crystals had been employed with great success to unravel the mysteries of crystalline structure; while in the hands of Moseley and his successors, the methods have been employed to determine the fundamental modes of vibration of the atoms, and to throw light on the constitution and the relation of the elements.

We now come to Moseley's most important discovery, with which his name will always be associated. To make matters clear, it is desirable to state briefly the theoretical position at the moment when he began his investigation. The writer had some time previously put forward the nucleus theory of atomic structure. On this view, the main mass of the atom is concentrated in a minute positively charged nucleus which is surrounded at a distance by a distribution of negative electrons to make it electrically neutral. This theory of atomic constitution was initially advanced in order to explain the remarkable large-angle scattering of swift a-particles in passing through matter. Geiger and Marsden carried out a detailed investigation of this scattering, and showed that the results were in good accord with the theoretical calculations based on the nucleus theory. It was deduced from the results that the atomic charge on the nucleus of an element increased with the atomic weight, and for the heavier elements, the number of units of charge was approximately equal to half the atomic weight of the element in terms of hydrogen. It was at the same time recognised that this value was only approximate, and could not hold for the lighter elements. General evidence indicated that the helium nucleus has two units of positive charge, and the nucleus of hydrogen only one. Van den Broek pointed out that the observations on scattering of a-rays were not inconsistent with the view that

the nucleus charge is equal to the atomic number, i.e., to the number of the element when arranged in order of increasing weight. This view, which had much to commend it, was adopted by Dr. Bohr in his work on the constitution and spectra of the elements. On the nucleus theory, the properties of an atom are determined almost entirely by the magnitude of the charge on the nucleus, since the number and arrangement of the external electrons, which control the main physical and chemical properties, are dependent on the magnitude of the nucleus charge, which can only vary by integral units. It was thus of fundamental importance to settle whether the properties of the atom are defined by the nucleus charge or atomic number rather than by its atomic weight.

Moseley determined to attack this problem directly, by comparing the X-ray spectra of a series of elements. As a preliminary, it was necessary to develop the photographic method of determining the X-ray spectra. fortunate in finding a particularly fine crystal of potassium ferrocyanide, which had a large and accurate face, and gave very good photographic definition in the third order of spectra. This was calibrated in terms of rock-salt, and was used in all his subsequent experiments. investigation he examined the X-ray spectra of a series of twelve successive For this purpose, specimens of these elements, from calcium to zinc. elements were arranged on a movable platform in a discharge tube, so that any element could be made an anticathode when required. The spectra of all these elements were found to be similar in type, and to consist of two Later investigation has shown that each of these lines in reality is a close doublet. It was found that the vibration frequency of the corresponding lines increased by marked and definite steps in passing from one element to the next. He showed that the frequency of the spectra was proportional to  $(N-a)^2$ , where N was a whole number and a constant of value equal to unity. This conclusion was of great importance, for it showed that the frequency of vibration depended on the square of a number which varied by unity in successive elements. He concluded that N corresponded to the atomic number of the element, and was equal to the number of units in the nuclear charge. Another interesting point came to light. It had long been known that the chemical behaviour of nickel and cobalt did not correspond with the order of their atomic weights. The results of the X-ray spectra, however, showed that cobalt had an atomic number 27 and cobalt 28, in the right order of their chemical properties.

Arrangements were then made to make a systematic determination of the X-ray spectra of the great majority of the solid elements. The spectrum of the "K" characteristic radiation was utilised for elements up to silver, but it was found difficult to excite this radiation strongly in the heavier elements. For elements of higher atomic weight, it was found simpler to determine the spectrum of the "L" characteristic radiation, as it was easily and strongly excited. The spectrum of this radiation showed in general five well-marked lines, but in some cases the radiation was so easily absorbed by matter that

it was necessary to use a very thin window for the escape of the rays, and also to keep the crystal and photographic apparatus in a vessel nearly exhausted of air to avoid absorption. A comparatively large window, covered with a thin goldbeater skin was used, and this often broke down and had to be replaced and the tube re-exhausted. Notwithstanding these difficulties, the work made very rapid progress, and Moseley determined the spectrum of 38 elements in all. The frequencies of corresponding lines in the "L" spectra were found, as in the previous case, to be proportional to  $(N-b)^2$  where N was the atomic number and b another constant of value 74. These results have been confirmed and extended to the heavier elements by the subsequent investigations of Siegbahn.

The power of this new method of attack is well illustrated by its immediate consequences. From a consideration of the atomic numbers to be allotted to all the known elements, Moseley was able to show definitely that only three possible elements had remained undiscovered between aluminium and gold. The X-ray spectrum of each of these missing elements can be predicted with certainty, so that the problem of search and identification should be much facilitated. There had long been much difference of opinion about the number of elements in the rare earth group; but the new method settled at once not only the number of elements but the X-ray spectra to be expected from each.

There can be no doubt that the two papers of Moseley on "The High Frequency Spectra of the Elements" published in the 'Philosophical Magazine' will become classical, for they contain a complete proof of a new relation between the elements of extraordinary interest and importance. The properties of an element are shown to be defined by a whole number which varies by unity from one element to the next, and the number is to be identified with the atomic number of the elements, and also with the number of units of electrical charge in the atomic nucleus. This number is more fundamental in fixing the properties of an element than its atomic weight. This proof of Moseley will, in my opinion, rank in importance with the discovery of the periodic law of the elements and of spectrum analysis, and in some respects is far more fundamental than either.

The fundamental importance of these discoveries was immediately recognised by the scientific world. Prof. Urbain, the well-known authority on the rare earths, visited Moseley at Oxford, and the latter was able to determine in a few days the actual elements present in Prof. Urbain's preparations, and to form an estimate of their relative proportion. No evidence was found of an element with an atomic number 61. Moseley gave an actount of these and other experiments on the rare earths before Section A of the British Association at Sydney, but it is unfortunate that no record of his definite conclusions on this question has been found. Before his departure to the Dardanelles, Moseley wrote to me that he intended to publish a note on these experiments. Apparently he found no time to do so, and a careful search of his papers has not given any definite information,

although all the photographs of the X-ray spectra have been preserved. It is hoped that Prof. Urbain will be able to publish later in some detail the bearing of Moseley's observations in his work on the rare earths.

I have the permission of Prof. Urbain to publish his letter sent to me on receiving information of the death of Moseley.

Paris, le 26 Septembre, 1915.

MON CHER COLLÉGUE.

La lettre que vous m'adressez et qui m'apprend la mort de Moseley me plonge dans la stupeur. J'avais été très surpris, lors de mon voyage à Oxford, de trouver un très jeune homme capable de faire un aussi remarquable travail.

Il avait rédigé ses notes—celles qui ont été publiées—avec une extrême modestie, reportant sur vous tout le mérite de la découverte de la loi qu'il avait porté à la connaissance du monde savant. L'importance de cette loi m'avait frappé, et je lui ai accordé, dès le début, une importance fondamentale, la faisant figurer parmi celles qui doivent être énoncées comme base du corps de doctrines de la chimie théorique.

Le premier, en France, j'ai enseigné la loi de Moseley. Je continuerai à la nommer ainsi et je m'efforcerai de la rendre classique.

M. de Broglie, qui a travaillé avec succès dans la même direction, lui attribue la même importance. . . .

Avec les quelques documents que j'ai rapportés d'Oxford et mes souvenirs, je pourrai sans doute reconstituer à peu près le travail que Moseley a fait sous mes yeux.

En gros, les résultats sont les suivants: Les éléments que la photographie a révélés, et qui figurent dans le groupe Ytterbique sont:—

Un seul Erbium.
Un seul Thulium.
Deux Ytterbiums { Neoytterbium.
Lutécium.

Le celtium n'a pu être révélé; toutefois, il reste dans la série de Moseley une place pour le celtium, entre le lutécium et le tungstène.

Ainsi la loi de Moseley, pour la fin du groupe des terres rares comme pour le commencement, consacrait en quelques jours les conclusions de mes efforts de 20 ans de patient travail. Ce n'est d'ailleurs pas cela qui me faisait admirer le travail de Moseley. Sa loi substituait à la classification un peu romantique de Mendeléeff une précision toute scientifique. Elle mettait du définitif dans la période des recherches hésitantes sur les éléments chimiques. Elle terminait un des plus beaux chapitres de l'histoire des sciences.

Ce sera là l'éternel honneur de Moseley, auquel s'ajoutera celui de sa mort glorieuse. . . .

G. URBAIN.

Moseley was one of those rare examples of a man who was a born investigator, and his remarkable record for four brief years' research led those who knew him best to prophesy for him a brilliant scientific career.

After a year's experience at research, he had developed into a rapid and skilful experimenter, and showed that combination of courage and ability so necessary for the attack of new and difficult problems. Endowed with unusual intellectual powers and equipped with a good mathematical training, he read widely and soon acquired an accurate knowledge of the problems of modern physics. His powers of continuous work were extraordinary, and he showed a predilection for turning night into day. When his researches were at an interesting stage, it was not unusual for an early arrival at the laboratory to meet Moseley leaving after about fifteen hours of continuous and solitary work through the night. His originality and unusual powers as an investigator were soon recognised by his co-workers in the laboratory, while his cheerfulness and willingness to help endeared him to all his colleagues.

Moseley was a clear and fluent speaker, and possessed to an unusual degree the power of picking out the essentials of a subject. In the first paper he read before the Royal Society, he was specially complimented by the then President, Sir William Crookes, on the admirable method of presenting the results of his work. All those who heard him join in the discussion on the "Structure of the Atom" before the Royal Society could not fail to be impressed by his clear, able, and yet modest presentation of his own fundamental contributions to that subject.

In private life he was a pleasant and genial companion with wide interests. He spent most of his vacations with his mother in their cottage in the New Forest, and was a keen gardener and a student of natural history.

It is a matter of great regret that the services of Moseley could not have been utilised for the war in some scientific capacity rather than as a combatant in the firing line. He offered his services freely to his country in the direction where there appeared to be the greatest need, and entered on his military duties with the same zeal as on his scientific work. In his letters from the East, we know that he cheerfully put up with the inevitable hardships of the campaign, and faced the future with courage and resolution.

By a soldier's will, made on active service, Moseley bequeathed all his apparatus and not inconsiderable private wealth to the Royal Society for the furtherance of scientific research. It is to be hoped that some way may be found of perpetuating the memory of such a gifted son of science who freely gave his life for his country's cause.

E.R.



Photo by Ellion & Fry, IAd

R. Meldola.

## RAPHAEL MELDOLA, 1849-1915.

RAPHAEL MELDOLA, son of the late Samuel Meldola, and grandson of Raphael Meldola, Chief Rabbi, was born in London, July 19, 1849. The Meldolas came of an ancient Sephardic family, the genealogy of which can be traced through sixteen generations without a break back to Isaiah Meldola (born 1282, died 1340), of Toledo. The name Meldola seems to have been assumed by some of the family who first established themselves in Italy at a place of that name not far from Ravenna. The Sephardim consist of the Spanish and Portuguese Jews, and form the moré aristocratic section of the race. Many of them were learned men, some practised medicine, and several wrote on mathematics, astronomy, and philology. The earlier members of the family for many generations were the Chief Rabbis of their communities.

Raphael received his early education in private schools, and entered the Royal College of Chemistry in 1866. He spent a short time as assistant in the laboratory of the late Dr. John Stenhouse, F.R.S., and he then entered the colour works of Messrs. Williams, Thomas, and Dower, of Brentford, where he remained about two years. In 1873 he rejoined the College, then transferred to South Kensington, and served for a time on the teaching staff under Prof. (afterwards Sir Edward) Frankland. At this time he was attracted by the study of spectrum analysis, and worked under the direction of Sir Norman Lockyer. In 1875 he was placed in charge of that portion of the Government Eclipse Expedition which went to the Nicobar Islands, but unfortunately bad weather interfered with the observations. On his return to England he was engaged as scientific chemist at the Atlas Colour Works at Hackney Wick (Messrs. Brooke, Simpson, and Spiller), and there he remained eight years. At this time he made a number of important discoveries in connection with coal-tar colours, which, however, received more attention in Germany than in this country. Thus, in 1879, he discovered the first oxazine dye-stuff, still generally known as Meldola's blue. was never manufactured in England, but was produced in large quantities in Germany under various names. Meldola also carried out a considerable amount of research on the triphenylmethane colours, much of which, however, was never published. He was also the discoverer of the first acid green (from benzaldehyde and diphenylamine) and of the beta-naphthalated rosaniline sulphonic acid, first brought out in 1883 as alkali blue XG, and which has recently become of considerable importance for cotton dyeing under the names of chlorazol, brilliant blue, isamine blue, brilliant sky blue, etc.

The investigations which he published, dealing especially with derivatives of naphthalene and with azo-compounds, appeared in the 'Transactions of the Chemical Society.' This work, for the most part overlooked in England, has

Disappointed by the small amount of borne extensive fruit in Germany. encouragement received from his employers, he accepted, in 1885, the post of Professor of Chemistry at the Finsbury Technical College, and thus relinquished direct association with the industrial application of chemistry. He did not, however, cease to take an interest in the manufacture of dyestuffs and in the applications of chemistry to industrial purposes in general. He never lost an opportunity of pointing out the disastrous consequences which would ensue, and which, as a matter of fact, have ensued in respect to the coal-tar dyes, from the neglect of science in this country. communicated to the Society of Arts, so long ago as 1886, sounded his first note of warning. The contention that the decline of the colour industry in England and its gradual transference to Germany were due to defects in our Patent law, or to the want of sufficient facilities for the use of duty-free alcohol by manufacturers, he showed to be almost entirely without foundation. And he proved in many papers, lectures, and addresses that the real cause of the loss to this country was the inability on the part of manufacturers to perceive the necessity of associating uninterrupted research with manufacturing operations, not only with the view to improvements in processes actually worked, but for the purpose of continually adding new products to those at the time available.

His reputation as one of the recognised authorities on the chemistry and manufacture of dyes explains his appointment in July, 1915, to the Chairmanship of the Advisory Council of British Dyes, Limited. He had, however, in a vigorous and characteristic letter to 'The Times' of January 20 of that year, protested against the constitution of a directorate in which scientific chemistry was unrepresented. His views on this subject can best be expressed by a few words from his last address to the Institute of Chemistry on March 1, 1915. "I repeat," he said, "it is not a business question, but a chemical question, and it is by chemical research alone that our colour industry can be saved in the long run. Consider the leeway that we have to make up. The German colour industry has been built up by the utilisation of the results of research earried on in the factories and universities and technical schools for a period of over forty years! To suppose that we can retrieve our position after forty years of neglect by starting a company, the directorate of which is to consist solely of business people is simply ludicrous." Again later, "The group of industries which have arisen from the products of the tar still are not going to remain stagnant after the war, and it is scientific guidance and not mere assistance that will keep them alive. It is the expert, and the expert only, who can foresee the course of development; who can keep in touch with the progress of research, and who can direct with intelligence the campaign against our competitors. If such scientific direction is withheld, all schemes are sooner or later bound to end in failure. I deliver my second warning to a new generation after an interval of about thirty years; if it is again unheeded, so much the worse for the country!"

As professor at the Finsbury College, where he held office from 1885 till

his death on November 16, 1915, Meldola was indefatigable as a teacher and in promoting the welfare and advancement of his students after leaving college. Of his success in this direction there is evidence in the fact that several of his past pupils became Fellows of the Royal Society and occupy University chairs. It is interesting in this connection to notice that the place left vacant at Finsbury will be occupied by a former student of his own, Prof. Gilbert T. Morgan, F.R.S.

Meldola's scientific chemical work related chiefly to synthetic colouring matters, and, as already mentioned, is recorded chiefly in the 'Journal of the Chemical Society'; but he was also an authority on photographic chemistry, and published a book on the subject in 1891. In 1904 he published, under the title, 'The Chemical Synthesis of Vital Products,' the result of several years of laborious compilation. He was, however, not a chemist only, for his earliest studies led him in quite a different direction, and it would seem that his own inclinations wavered between chemistry, which became his professional occupation, and natural history, which filled his scanty leisure. The first six papers under his name in the Royal Society Catalogue relate to biological subjects, among which is prominent the protective mimicry found among insects. This subject he pursued with success, and after taking a leading part in starting the Essex Field Club in 1880, he became President of the Entomological Society in 1895. In 1882, encouraged by Darwin, he translated Weismann's 'Studies in the Theory of Descent.'

During the latter part of his life, Meldola gave much time to the work of the several societies connected with chemistry. In turn he became President of the Chemical Society (1905-7), the Society of Dyers and Colourists (1907-8), the Society of Chemical Industry (1908), and the Institute of Chemistry (1912-15). With regard to the last-named institution, Meldola, though one of the original Fellows, was not at first enthusiastic about the Institute and its work, but in course of time he became convinced that it had a public mission to fulfil of the same order of importance as that discharged by other bodies of professional men. As President, at the end of his first year of office, he used the opportunity to acknowledge this alteration of his views. He was also instrumental in arranging a conference of professors of chemistry and other teachers with the object of bringing the training and examinations prescribed by the Institute for its Associates into more harmonious relation to the work of the Universities, and there can be no doubt that this closer connection will hereafter operate beneficially on all the institutions in which young chemists are educated with a view to the practical application and utilisation of their knowledge.

Meldola received many scientific honours. He was elected into the Royal Society in 1886. He served twice on the Council of the Society (1896–1898 and 1914–1915), and in 1914 was appointed a Vice-President. He had been nominated again for a seat on the Council for the year 1915–1916, shortly before his death. In 1910 he was awarded the honorary degree of D.Sc. by the University of Oxford on the occasion of his Herbert Spencer Lecture; he

also received the LL.D. of St. Andrews in 1911. The Royal Society awarded him the Davy Medal in 1913. He also twice received the Albert Medal of the Society of Arts, in 1886 for a paper on the "Scientific Development of the Coal Tar Industry," and in 1901 for a paper on the "Synthesis of Indigo." The French Chemical Society awarded him their Jubilee Medal in 1911, and in the same year he received a gold medal from Turin, in recognition of his scientific publications.

In 1886 Meldola married Ella Frederica, daughter of the late Dr. Maurice Davis, J.P., who survives him. His end was quite sudden, and may be ascribed, with great probability, to the effect of overwork following on an illness which in the previous spring had involved a troublesome surgical operation. But Meldola was not one to spare himself when he heard the call of duty, and since the outbreak of war his work on various committees had been incessant.

It would not be easy to do justice to Meldola's personal character, on account partly of his natural modesty, partly on account of his many-sidedness. He was a good chairman, always clear, judicious, tactful, and good-humoured. His friendships once formed remained unbroken through long years to the end, and this is perhaps the best testimony to the quality of his heart.

W. A. T.

Raphael Meldola was unique in the breadth and depth of his scientific knowledge. Amid all the ever-increasing specialisation of our age, "he kept alive and fresh every one of the diverse interests that had appealed throughout his life to his many-sided intellect; by sure scientific insight he spoke with authority on them all." The scientific reviews written by him deal with works in various different departments of the following subjects: Chemistry, organic, inorganic, and industrial; Astronomy; Photography; Natural History; Anthropology; Evolution; Government in its relations with Science; and the same breadth is illustrated by the scientific committees of the British Association, on which he served for many years.

The recognition of Meldola's far-reaching powers implied in the above statements was, of course, based on his original contributions to learning. The researches of a single year will afford sufficient evidence of the extraordinary range of his intellect. In 1882 he published "Contributions to the Chemical History of the Aromatic Derivatives of Methane,"† "Mimicry between Butterflies of Protected Genera,"‡ and with General Pitt Rivers and W. Cole he issued a "Preliminary Report of the Committee appointed to investigate the Ancient Earthwork in Epping Forest, known as the Loughton Camp."§

<sup>\* &#</sup>x27;Nature,' vol. 96, p. 347 (1915-16).

<sup>† &#</sup>x27;Trans. Chem. Soc.,' vol. 41, p. 187.

<sup>† &#</sup>x27;Ann. Mag. Nat. Hist.,' Dec., p. 417.

<sup>§ &#</sup>x27;Rep. Brit. Assoc.,' p. 274.

I have never met anyone—only intimate friends can have known it fully—who was more alive to the human associations in which, happily for us, the science of our day is so abundantly rich. In other ages other intellectual activities held sway: in our own age science, being the spirit of it, is richest in human associations. Those who have stood in the way in the early years, when an awakening interest may be helped or thwarted, can never have realised their responsibility. But how great it is !—the responsibility of encouraging or of hindering a young man on his way to join the great and varied army that is pushing on into the unknown, and is doing the real inspiring work of the world. Think of all that he may lose, not only of work but of comradeship, of how, in being forced, against his inclination, to study the "humanities," he may miss his best chance of knowing man himself.

Meldola's former pupils, whose first original work was done with him, and who have now risen to eminence, have told\* of all that he was to them. In the intimacy of our long friendship I was permitted to see the other side and to know what they were to him—how he valued his association with them and all who helped him in his work, how anxious that justice should be done them when they had left him to make their own way in the world.

Meldola kept the same love for the human associations of natural history throughout his life. With him collecting was always a social pursuit, and each prize had its own special memories. He would speak with delight of a very rare moth† captured by his mother at Deal, of a unique variety‡ of a common moth found by his wife.

The happiness of Meldola's married life was heightened by common interests. His wife was not only the companion who collected with him in summer vacations, but the friend who entered into every side of his life, who sympathised with him in all his work, and delighted to know that her sympathy was an encouragement, and that she could give him practical help as well. For all the typewriting of his work was done by her.

Meldola's strong bent towards natural history appears in his earliest publications, of which the first, a note on "Fascination Exercised by a Frog," appeared in 1869, soon followed by an observation on the British moths, which were to provide him with one great interest and his chief recreation throughout life. Many other articles and notes followed, and in three or four years it had become clear that his chief biological interest lay in the study of evolution in relation to insects. The limits of space prevent me from referring to many of his publications on this subject, but there are

<sup>\*</sup> See 'Raphael Meldola,' Williams and Norgate, London, 1916.

<sup>+</sup> Nonagria sparganii, captured in a back garden. 'Entomologist's Monthly Magazine,' vol. 21, p. 135 (1884-85); 'Entomologist,' vol. 17, p. 253 (1884).

<sup>1</sup> August 12, 1912: on a mossy wall at Dunbar.

<sup>§ &#</sup>x27;Entomologist,' vol. 4, p. 232 (1868-9).

<sup>|</sup> Ibid., p. 303.

some which cannot be omitted in any adequate account of the man and his work.

In a paper published by the Zoological Society in 1873, "On a Certain Class of Cases of Variable Protective Colouring in Insects," he argued for "a power of adaptability on the part of each individual"—a power which he contended was conferred by natural selection. This paper was the foundation from which sprang a large amount of work, which he followed with keen interest and sympathy. "Entomological Notes Bearing on Evolution" † appeared in 1878, founded on Fritz Müller's letters from Brazil. He here dwelt on the bionomic importance of habits, and their evolution through natural selection—a subject which always retained his interest. His first Presidential Address to the Entomological Society in 1896;—"The Speculative Method in Entomology"—was a defence of the "scientific use of the imagination" in this science.

Meldola also took an active part in discussion, in the columns of 'Nature,' on subjects connected with organic evolution. In 1888 he wrote on "Lamarckism versus Darwinism" (vol. 38, p. 388); in 1891 on "Co-adaptation" (vol. 43, p. 557; vol. 44, p. 7); in 1896 on "The Utility of Specific Characters" (vol. 54, p. 594; vol. 55, p. 29)—a subject to which he devoted his second Presidential Address to the Entomological Society, "The Utility of Specific Characters and Physiological Correlation."§

One of the dominant influences on Meldola's life was his 11 years' friend-ship with Charles Darwin, for whom he always felt the strongest affection and veneration. I remember his pleasure in recalling a remark made to him by Darwin concerning Nature, the Great Incorruptible—"She will tell you a direct lie if she can!" And he told with hearty laughter of Darwin's gardener, who was so disappointed when the experiments behaved properly, contrasting his delight at a failure with his grudging admission of success.

Meldola was secretary of the Entomological Society of London from 1876 to 1880, and Darwin was accustomed to refer to him the observations on insects made by Fritz Müller in Brazil. A warm friendship sprang up in this way between Meldola and the great German naturalist, many of whose observations were published in this country. Meldola always thought that Fritz Müller ought to have been an early recipient of the Darwin Medal of the Royal Society, and it is probable that many naturalists felt the same when it was too late. Among Meldola's greatest friends were Wallace, Bates, and Trimen, his seniors, as was Fritz Müller, in the important department of evolution that he made his own.

Darwin's correspondence with Meldola is chiefly concerned with mimicry

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* 'Proc. Zool. Soc.,' p. 153.
+ 'Ann. Mag. Nat. Hist.,' 5 ser., vol. 1, p. 155 (1878).
† 'Proc. Ent. Soc. Lond.,' 1895, p. 48.
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<sup>§</sup> Ibid., 1896, p. 64.

Published in 'Charles Darwin and the Theory of Natural Selection,' chap. xxv, pp. 193-218 (1896), Poulton, London.

and allied subjects, and with the English translation of Weismann's 'Studies in the Theory of Descent,' published in 1882. Darwin had been greatly impressed by the German original, and in 1877 wrote about it to Meldola, offering to lend him the book. Later on he expressed the opinion that it would be "a public benefit to bring out a translation," and in 1878 agreed to write a preface—although "this is a kind of job which I do not feel that I can do at all well and therefore do not like; but I will do my best." Darwin's last letter, written February 2, 1882, only a few weeks before his death on April 19, expressed the generous wish to be allowed to subscribe towards the cost of the work if any loss should be incurred by Meldola himself. No one who studies this volume can fail to recognise the great additional value it has gained from Meldola's editorial notes.

It was due to Meldola that the English statement of Müllerian Mimicry appeared only a few months after the German.\* But he did far more than bring out the translation; he defended the hypothesis in controversy and brought new and important classes of facts to confirm it. Meldola was the first to point out that Müller's hypothesis was supported by the strong resemblances that ran through the great groups of distasteful butterflies which supply the vast majority of the models.

"The prevalence of one type of marking and colouring throughout immense numbers of species in protected groups, such as the tawny species of Danais, the barred Heliconias, the blue-black Euplœas, and the fulvous Acræas, is perfectly intelligible in the light of the new hypothesis."

Meldola's suggestion, given in his own words in the above paragraph, opened up a new and fruitful field in which much research is still being carried on. Perhaps the most interesting development is the recognition of mimetic resemblances between distantly related groups of stinging insects—wasps, bees, and their allies—a study only just beginning, in which great advance is sure to be made.

The biological work, of which a brief account has been given above, formed the ground on which Meldola was proposed by Charles Darwin for the Fellowship of the Royal Society. He was elected in 1886, after too long an interval, as many thought at the time and all will acknowledge now. His claims would probably have been recognised earlier if they had been strong in only a single scientific subject instead of being strong in many.

The successful foundation and development of the Essex Field Club, in which Meldola took an important part, led him to think and write on many subjects which fell within the sphere of operation of this and similar societies.

<sup>\* &#</sup>x27;Proc. Ent. Soc. Lond.,' 1879, p. 20, translated from 'Kosmos,' May, 1879, p. 100. Fritz Müller, however, had published in the previous year a brief account of his hypothesis in 'Zool. Anzeiger' (Carus), vol. 1, pp. 54, 55 (1878). It is probable that he had not sent a copy of this preliminary statement to Darwin, for Meldola told me that he had never heard of it. It is now published, translated by E. A. Elliott, in 'Proc. Ent. Soc. Lond.,' 1915, pp. 22, 23.

<sup>† &#</sup>x27;Ann. Mag. Nat. Hist.,' 5 ser., vol. 10, pp. 417-425 (1882).

Thus—to mention but a single example—in 1883 he initiated a valuable movement by a letter to 'Nature' on "Local Science Societies and the Minor Prehistoric Remains of Britain" (vol. 29, p. 19), in which he argued that such societies should keep vigilant watch and prepare maps and other records.

Meldola's work for the Essex Field Club and kindred societies is but one striking example of a fine public spirit that was manifest throughout his whole career, from 1867, when, soon after leaving school, he delivered free lectures to Jewish working men, thus starting a movement which developed into the first Jewish working men's club. It is greatly to be hoped that his addresses, articles, and letters on science and industry, and on scientific and technical (including agricultural) education, may be published in a collected form without delay. They would be of the utmost value in preparing for the period of reconstruction that is before us. He has gone, but his teachings remain, and it is for us to make use of them.

The outbreak of war found this country in an extraordinary and difficult position. In August, 1914, the nation suddenly awoke to realise the dangers into which it had been allowed, nay, encouraged, to drift—with important industries, formerly flourishing, represented chiefly or entirely by crowds of clerks ordering goods from a foreign land. And that foreign land had, in an instant, become the bitterest, most unscrupulous and ruthless foe ever encountered in our long national history. In this crisis Meldola's remarkable knowledge and wide experience of the sciences that form the foundation of the industrial arts was of inestimable value. He saw the need, and, suffering as he was from the strain of overwork and far from strong, threw himself, heart and soul, into his country's cause. As early as August 29, 1914, while on his holiday in Scotland, he wrote to a colleague: "I think of preparing a general plan of campaign for recovering British chemical industries lost through German competition."

Soon after his return, on September 22, 1914, Meldola presided at a joint meeting of the Councils of the Institute of Chemistry and the Society of Public Analysts to consider the supply of laboratory requirements. A special committee on laboratory reagents, and another on glass,\* porcelain, and filter-paper, were the result. The last meeting he attended at the Institute was in connection with the Glass Research Committee, and he called with reference to its work only three days before he died.

In addition to all this work at the Institute, Meldola was one of the first to suggest to the Board of Trade the appointment of the Chenical Products Committee, of which he became a member; he was Chairman of the Advisory

<sup>\*</sup> Meldola wrote to me, October 28, 1915: "A striking example of the result of applying science is the development of the German optical and chemical glass industry, all of which at the time of the war was in the hands of our enemies." An excellent summary of the work of the Glass Research Committee of the Institute of Chemistry is given in 'The Engineer' of March 24, 1916, p. 249. In drawing up this brief account of Prof. Meldola's work at the Institute, I have received much kind help from the registrar and secretary, Mr. R. B. Pilcher.

Council of British Dyes, Limited, created by the Government to deal with another vast industrial failure; and he held a place on the Council of the "Scheme for the Organisation and Development of Scientific and Industrial Research," a belated attempt by the Government to atone for past neglect.

When the call of his country came Meldola was ready, and he worked beyond his strength.\* England has never had a more loyal or devoted son; he gave up everything for her in the hour of need. And what had the Government of England done for him? Meldola was twice offered a decoration of the Legion of Honour-in 1900 and again in 1907. occasions the Foreign Office forbade him to accept the distinction. Can we seriously suppose that it was the wish of Lord Salisbury in the earlier year or of Sir Edward Grey in the later, thus to treat a friendly nation,† and the eminent man she desired to honour? No, the cause of the intolerable disgrace must be sought in some wooden system erected by the permanent service—one of many unheeded warnings of disaster and misery that were so soon to follow in the train of official ignorance of science and official contempt for those who devote their lives to science. It is not to be supposed that scientific men more than others value such distinctions; indeed, with so much of absorbing interest to occupy their minds, they are less likely to think too much of them. But, of course, the token of appreciation by foreign scientific colleagues is peculiarly gratifying, and in this instance it was especially so, for, next to his own country, Meldola had always held France to be the dearest land of all.

I dwell here and now on the incredible meanness with which scientific men are treated by a Government Department, because it is the clear duty of the Royal Society, so often appealed to by the Government, to protest, nay, more than protest, to ensure that the possibility of such a disgrace in the eyes of the intellectual world which stupid officialism has inflicted upon our country shall be forthwith removed.

This is but one change which surely cannot be delayed, but how many and great are the necessary reforms which rise before us as we think of the life and teaching of the great man we have lost, just when we needed him most! In the steadfast hope, which was also his, that the country will learn the lesson before it is too late, I conclude with words which Meldola had specially noted down so that they might live in his memory:—

"While men strive, and fail, and faint by the way, the work they have tried to do does not fail, but is eternally carried on in ways unknown to them."

E. B. P.

<sup>\*</sup> On October 28, less than three weeks before his death, he wrote to me:—"I am still insomnolent and depressed, and overwhelmed with work, and every post brings in shoals of letters requiring more and ever more correspondence."

<sup>†</sup> Meldola wrote to me concerning the 1907 incident: "The Chemical Society of France, on whose recommendation the distinctions were offered, thus received a direct snub from this country."

<sup>!</sup> From 'Knight-Errant,' by Edna Lyall.

### BENJAMIN WILLIAMSON, 1827-1916.

BENJAMIN WILLIAMSON was born on January 9, 1827. He was the third son of a country clergyman, the Rev. Benjamin Williamson, Rector of Mourne Abbey, co. Cork. He is thus one of the many men of high intellectual attainments who have come from the quiet precincts of a country vicar's family. One, at least, of his father's predecessors had been a man of action. There is a record of brilliant military distinction attached to a Lieutenant Richard Williamson, who in 1641 made a gallant defence of the North Castle of Mallow (co. Cork), when this was assaulted by Lord Mountgarret, commanding the rebel forces at that period. The Rev. Benjamin Williamson claimed descent from this brave young soldier. It seems probable that, from the mother's side, the subject of this memoir derived some part of his mathematical talent. Abigail Roberts, mother of Benjamin Williamson, was, in fact, a member of a family which at a later date showed distinguished mathematical gifts. Her family gave three Fellows to Trinity College, all possessed of remarkable mathematical gifts, and who by their writings have contributed to the advance of that science.

Not many miles from Mourne Abbey, and in the near neighbourhood of the beautiful town of Mallow, the Rev. Benjamin Williamson possessed a property known as Old Dromore. The house, standing on an elevation, looks over a richly wooded country. Everything here suggests peace and retirement, the sequestration from even the traffic of country roads, the silent and shady walks, the quiet waters of a secluded lake deeply hidden among trees. In these scenes young Williamson passed much of his boyhood. And here the writer of this notice found the old man—in heart still a boy—walking through the woods, keen in the enjoyment of nature, although in his 86th year.

His early education was received at Kilkenny College, and, upon attaining the age of 16 (on October 13, 1843), young Williamson matriculated in Trinity College, Dublin. It was his lot to be closely associated with that institution for the ensuing 73 years.

During his undergraduate years Williamson gained many distinctions, culminating in a First Senior Moderatorship in Mathematics in 1848. His tutor was his kinsman, the Rev. William Roberts, a brilliant scholar and a most kindly man, whose influence upon the young student must have been considerable. The close of his student days saw Williamson endowed with the friendship of many contemporaries destined to make a name for themselves, such as Morgan W. Crofton, G. Johnston Stoney, and James Murphy, of legal fame. And in these friendships he found probably a spur to further exertions. His reading was steadily continued, and four years later—in 1852—he won the coveted prize of Fellowship. It is to be remarked that in those days the contest for this valuable distinction was not so severe an

ordeal as it became in later times. Williamson became a tutor of his college seven years later.

From the date of his election to Fellowship his life ran in the peaceful channels of scholarship. Year after year there came and went the various mathematical classes which he was appointed to teach, and year after year the number of those who looked back with pleasure and gratitude to his patient and kindly help went on increasing. No man ever gained more friends. Of a life so blessed with peaceful study, there are no incidents to relate other than those arising from his mental activity.

His earliest published paper appears to have been one "On the Solution of Certain Differential Equations," which appeared in the 'Philosophical Magazine' for 1856 (vol. 40). This is a brief contribution, extending a general method in analysis, due to Boole, to the reduction of certain classes of differential equations. Two other short papers stand to his name in the Royal Society's Catalogue. One "On Gauss' Theorem of the Measure of Curvature at any Point of a Surface" ('Q.J. Math.,' vol. 11, 1871), and one. "On the Conditions for a Maximum or a Minimum in a Function of any Number of Variables" ('Q.J. Math.,' vol. 12, 1873). There is also a paper on "Curvilinear Co-ordinates" in the 'Royal Irish Academy Transactions.'

Williamson's treatise on the Differential Calculus was first published in 1871 and that on the Integral Calculus in 1874. He was thus in middle age when these well known works appeared. Distinctions followed the appearance of these books. In 1879 he was elected a Fellow of the Royal Society. In his own University he was in the same year Donegal Lecturer in Mathematics, and in 1884 became Professor of Natural Philosophy. The Degree of D.Sc., then newly established in the University of Dublin, was conferred upon him in 1891. He received the D.C.L. of Oxford in 1892.

By seniority he became a Senior Fellow of his College in 1897. In this capacity he retained a seat upon the Board till within a few months of his death, which occurred on January 3, 1916.

Benjamin Williamson's claim upon his contemporaries, and upon his successors, undoubtedly lies in these two works: the treatises on the Differential and upon the Integral Calculus. Their clearness and elegance of style have been so generally recognised that any prolonged reference to them here is quite superfluous. Their circulation, for books of the kind, was most remarkable. The treatise on the Differential Calculus went through eight editions between 1871 and 1892, and the ninth appeared in 1900. The treatise on the Integral Calculus also attained many editions, the eighth appearing in 1906. It would be difficult to appraise the value of the educational work which these books have accomplished, not only among students, but as serving for groundwork and models for other works on the subject. They have not been surpassed by any works of the same scope.

Williamson also wrote, in conjunction with Dr. F. A. Tarleton, Fellow of Trinity College, 'An Elementary Treatise on Dynamics; containing Applications to Thermodynamics.' This appeared in 1885 and has seen a

second edition. Still later, in 1893, he wrote 'An Introduction to the Theory of Stress and Strain.' To the 'Encyclopædia Britannica,' 9th edition, he contributed articles on the Infinitesimal Calculus, the Calculus of Variations, and on Colin Maclaurin, etc.

That Benjamin Williamson's name will long survive as of one brilliantly associated with the spread of mathematical knowledge in English-speaking countries is certain. We may say with safety that no one of his contemporaries has done more towards the attainment of that great end. While the educated public can appraise the justness of this claim from a knowledge of his published mathematical work, Williamson's work as a class teacher can only be estimated by those who—like the present writer—came under his instruction. Nothing more admirable for clearness, method, and unwearying patience, can be conceived. His lectures were, in the present writer's opinion. models of what such lectures should be. But it was not only in powers of exposition that Benjamin Williamson excelled as a teacher. The more diligent student found in him a sympathy and a personality which invited friendship and affection in an extraordinary degree. No more genial and kindly man ever breathed, and none more sympathetic to every claim for help and assistance. In old-world dignity and courtesy he recalled the best type of Irish country gentleman—a type which, alas! seems to be disappearing in our times.

One side of Williamson's work must not be left unnoticed: his work for his College and University. With him the interests of this great undivided institution claimed a devotion almost religious in intensity. No pains were too great, no exertion spared, where its interests were concerned. devotion showed prominently in the recent movement for the betterment of the scientific schools of the University. For many years the neglect of the Departments of the Natural Sciences was a hindrance to all advance. Men such as G. F. Fitzgerald and C. J. Joly struggled in vain after reform. 1903 an appeal was issued by the Chancellor (the late Lord Rosse), the Provost (the late Dr. Salmon), and other friends of the University, with the intention of erecting and equipping science laboratories in Trinity College. In this movement Williamson took on himself the onerous duties of treasurer. For a period, in spite of the generous help of the Chancellor, it looked as if the movement must end in comparative failure. The intervention of Lord (now Viscount) Iveagh in recognition of the claims of science upon the older Universities, changed the course of events. To-day the splendid and well endowed laboratories of Experimental Physics and Botanical Science, as well as a research staff to aid the School of Geology, are the tangible results. Among those who month after month and year after year bore the toil associated with the collection and disbursement of the large sums involved, none did more conscientious work than the subject of this memoir. Before his death he presented a valuable collection of scientific and mathematical books to the Department of Geology.

Benjamin Williamson lived to a great age in the midst of the affection and

respect of all who knew him. To the last his friends were welcomed to his house with the old characteristic kindness and courtesy, the old geniality and sympathy.

He married Agnes, daughter of the Rev. W. Wright, Vicar of Selston, Nottingham, who died in 1899. He leaves one daughter, who is married to William Henn Hinde, M.Inst.C.E.

J. J.

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#### SIR JAMES STIRLING, 1836-1916.

THE RIGHT HON. SIR JAMES STIRLING was the eldest son of the Rev. James Stirling, Minister of the George Street United Presbyterian Church, Aberdeen. He was born at Aberdeen on May 3, 1836. After passing through the Grammar School and University of his native city, he entered at Trinity College, Cambridge, and in 1860 was Senior Wrangler and First Smith's Prizeman. In 1862 he was called to the Bar at Lincoln's Inn. He was appointed a member of the staff of the Law Reports in 1865, and continued to act in that capacity, as a reporter in the Rolls Court, until 1876. He acquired a considerable reputation as a practitioner at the Chancery Bar, and in 1881 became Junior Counsel to the Treasury. He never "took silk," but passed from the Junior Bar to the Judicial Bench in 1886, when he was appointed a Judge of the Chancery Division of the High Court. In 1900 he was promoted to be one of the Lords Justices of Appeal. In 1906 he retired from the Bench. As a Judge he was, though somewhat slow, learned, painstaking, and accurate; and his judgments, which were models of lucidity, were seldom reversed. He was considerate and courteous, and was much esteemed by the Bar.

Sir James was elected a Fellow of the Society on April 24, 1902, as a member of the Privy Council. On his retirement from the Bench in 1906 he became able to take an active part in the business of the Society, and in December of that year he was appointed a member of the Finance and Scientific Relief Committees. He remained a member of the former Committee, and was a regular attendant at its meetings, until his death. He was appointed Chairman of the Scientific Relief Committee in December, 1908, and held the office for three years. He served on the Council from 1908 to 1910, and was a Vice-President in 1909 and 1910.

In February, 1914, he contributed a paper to the 'Proceedings,' vol. 90, A, p. 237, "On a Functional Equation employed by Sir G. Stokes."

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He was a M.A. of the University of Cambridge, and LL.D. of the University of Aberdeen.

He married in 1868, Aby, the daughter of Mr. J. T. Renton, of Shalford, Surrey, and had one son, who is a member of the Chancery Bar, and two daughters.

He died on June 27, 1916, at his residence, Finchcocks, at Goudhurst, Kent.

A. B. K.

#### SIR WILLIAM RAMSAY, 1852-1916.

By the death of Sir William Ramsay, England has lost one of her most distinguished chemists. From the times when Chemistry emerged from Alchemy, Great Britain has always produced in every generation at least one chemical investigator who has made great and fundamental discoveries—discoveries that have enlarged our ideas of chemical science, and have made the discoverer famous. Such an investigator was Sir William Ramsay. His work on the rare gases of the atmosphere, and on the production of helium by the spontaneous decomposition of the emanation of radium, will always mark an epoch in the history of chemistry.

Sir William Ramsay was born in Glasgow in 1852. He was the only son of William Ramsay, C.E. His grandfather was a dyer at Haddington; but in 1780 he left his dyeworks at Haddington to become a partner in the firm of Arthur and Turnbull, at Camischie, who manufactured various chemicals used by dyers. Wood vinegar, lead and aluminium acetates were amongst the substances produced, and later potassium bichromate was added to the list. It is probable that both potassium bichromate and a chrome orange dye were discovered by him. Another dye first produced by this firm was Turnbull's blue, and Sir William Ramsay believed that it was his grandfather who also discovered this compound.

His grandfather was the first and only president of a Chemical Society founded in Glasgow in 1798, of which Charles Tennant was also a member, but in 1801 a larger society, the Philosophic Society, was founded, and in it the Chemical Society was absorbed. His grandfather also corresponded with many of the best known French chemists, Vauquelin, De Morveau, and others, and Gay Lussac, when he passed through Glasgow on a tour to the Highlands of Scotland, spent a night with him. He died in 1827, leaving three sons and a daughter: Sir Andrew Ramsay, F.R.S., for many years head.

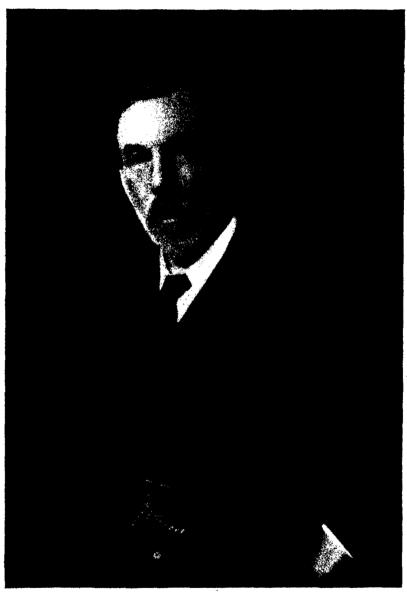


Photo by Efflott & Fry. Ltd

William Ramsony.

of the Geological Survey of Great Britain; John Ramsay, who was a sugar manufacturer in Demerara; Eliza Ramsay, who was an enthusiastic botanist, and who made various collections of the local flora in many parts of Scotland; and William Ramsay, the father of Sir William Ramsay.

William Ramsay was only 15 years old when his father died in 1827. A few years later Thomas Graham asked him to become his assistant at the Mechanics' Institute, but he went to the shipbuilding works of Robert Napier instead, and spent five years there. Later he took an active part as engineer, in the great railway development of those times, and finally became a local manager of the Scottish Union Assurance Society. He was not a professional scientist, but he had a good knowledge of science generally, and was especially a good mathematician.

Sir William Ramsay's mother, Catherine Robertson, came from an Edinburgh family, amongst whom were several medical men of note. Ramsay was a firm believer in heredity, and he certainly was descended on both the paternal and maternal side from ancestors who were much above the average in scientific and general intellectual power; and he used to say that "he had received as an heirloom his chemical endowment from his ancestors on both sides of the family."

From his fourth to his tenth year he went to an elementary school, the next five he spent at the Glasgow Academy; it was during the last year there that he was introduced to science. He then matriculated in November, 1866, in the University of Glasgow. His course of study there was the usual one, classics, general literature, logic, and mathematics. In 1869 he went to the chemical laboratory of Robert Tatlock, where he began chemistry Some years before, whilst he was at school, he had read Graham's 'Chemistry,' but it was chiefly for the purpose of learning how to make fireworks. He soon became Tatlock's assistant. In 1870 he attended Anderson's lectures on Chemistry, Alan Thomson's on Anatomy, and Lord Kelvin's (then William Thomson) on Physics. For six months he worked in Lord Kelvin's laboratory. The first work he had to do was unrolling and taking out the kinks from a great mass of copper wire, an operation that took nearly a fortnight; but, as Sir William Ramsay said, he learnt more in that six months unrolling copper wire and working with Kelvin's electrometer than any systematic course on Physics could have taught him.

At the end of the session he intended to work under Prof. Bunsen, in Heidelberg, but the Franco-Prussian War stopped him. After the war was over he went to Heidelberg, but in the spring of 1871 changed to the University of Tubingen, and entered the laboratory of Prof. Fittig. Here he started a research on platinum-ammonium compounds, and later on toluic acid. After two years he obtained the degree of Ph.D. He then returned to Glasgow, and took the post of assistant in the Young Laboratory of Technical Chemistry. In 1874 he became the assistant of Prof. Ferguson, in the University of Glasgow. Although most of his time was taken up by teaching large classes of medical students, yet he at once plunged into

scientific research with all the enthusiasm that in after years became more and more marked. From 1874 to 1880 (when he left Glasgow), he ranged over various fields in chemistry: he investigated a new bismuth mineral; the action of heat on ethyl-sodium-thiosulphate, thereby proving the constitutional formula for sodium dithionate; the physiological action of various anæsthetics, Sir William Ramsay himself being the corpus vile on whom the experiments were made; the production of various pyridinic acids by the oxidation of the pyridine bases that had been prepared 30 years before by Prof. Anderson; the synthesis of pyridine itself from hydrocyanic acid and acetylene; and in conjunction with J. J. Dobbie he noticed that the silver salts of some of the acids obtained by the oxidation of the alkaloids quinine. and cinchonine gave pyridine on heating, and were similar to the acids he had obtained by the oxidation of Anderson's pyridine bases; this was the first observation connecting that important class of organic compounds, the alkaloids, with pyridine, and marks an important discovery, for at the present time one of the definitions of an alkaloid is that it is a derivative of pyridine.

Early in 1880 he was appointed Professor of Chemistry at University College, Bristol, and the real work of his life began. In those days University College, Bristol, was a struggling institution, and needed a firm hand to guide it through a period full of trouble. Practically none of the other colleges that have since been founded were even thought of in those days, and the British public had but small interest in university education. Almost directly after he went to Bristol he was elected Principal of the College, and it was largely due to his patience and tact that many storms were successfully weathered, and that when he left Bristol in 1887 the College was in a more flourishing condition than he had found it.

Sir William Ramsay's life at Bristol was one full of hard work, but he was young, enthusiastic, and eager not only to help the College in every way as Principal, but also to add to its reputation by publishing as much original work as possible. It was also soon after he came to Bristol, in 1881, that he married Margaret Buchanan (the daughter of George Stevenson Buchanan, of Glasgow). Almost all the scientific work he did during his stay at Bristol was of a physico-chemical nature; Dr. S. Young, his assistant, collaborated with him, and the majority of the papers published were in their joint names. Together they covered a very wide field; vapour densities, thermal properties, evaporation, dissociation, critical points, were investigated, and many new and interesting observations were made. In order to carry out this work, all kinds of novel apparatus had to be devised, with the result that Ramsay soon became an expert glass blower, making many of the vessels necessary for the successful prosecution of the researches. Some of these inventions are now in common use in laboratories: to mention one, a jacketing tube and bulb, into which liquids of known boiling point can be introduced, so that, by surrounding a jacketed inside tube by the vapour of the boiling liquid at various pressures, definite constant temperatures can be obtained. Dr. Young and Sir William Ramsay worked out a series of substances, so that, by their use, any desired temperature between that of the atmosphere and 360° C. might be easily produced.

In 1887 Sir William Ramsay was chosen to succeed Prof. Williamson in the Chair of Chemistry at University College, London, where he worked for over twenty-five years. His activities, to start with, were along the same lines that he had followed in Bristol, and several important papers on molecular surface-energy were published. But soon he was led into entirely new country, where he made his greatest scientific discoveries. As so often happens, at any rate, in chemistry, a chance observation led to the most unexpected results. Lord Rayleigh, who had been making the most exact determinations on the densities of various gases, noticed that the density of pure nitrogen, prepared from the air by absorbing all known gases present, except the nitrogen, differed from pure nitrogen prepared from chemical compounds. The amount was excessively small, a figure in the third place of decimals; whilst a litre of chemically pure nitrogen weighs 1 2505 grm., a litre of nitrogen from the air was found to weigh 1 2572 grm. But Lord Rayleigh knew that the difference was larger than the error of experiment, and naturally was puzzled with the fact. He consulted several of the leading chemists, and received very little help; it is probable that, less than a year later, some of them must have felt keen disappointment that they had not accepted Lord Rayleigh's suggestion to help him to explain the curious anomaly. For Lord Rayleigh was offering to them the discovery of a new element-argon. Also, as it afterwards happened, four other new elements as well. But, when he sought help from Sir William Ramsay, he came to one who was willing at once to attack the problem, and one who was an expert experimentalist, never afraid of any difficulties, and, at the same time, full of enthusiasm to find out the solution of the puzzle.

After a few months of joint work, the startling announcement was made at the British Association Meeting at Oxford in 1894, that there was present in the atmosphere a gas new to science, and probably an element, for it yielded a spectrum entirely different from any known spectrum. This gas was afterwards named Argon. But chemists are, as a rule, conservative, and, although this discovery was vouched for by two such expert scientists as Lord Rayleigh and Sir William Ramsay, yet many looked on with incredulity. But not for long, for in the winter the full research was given in a paper to the Royal Society, and it was proved beyond all doubt not only that argon was a new element, but that it differed from all known elements, being entirely inert, and refusing to form compounds with any known substance.

Almost immediately after this, another chance observation led to momentous results in the hands of Sir William Ramsay. Sir Henry Miers noticed in an American geological journal a paper by Hillebrand, where it was stated that a rare mineral—cleveite—when heated gave considerable quantities of gas. Hillebrand was under the impression that the gas was nitrogen. Sir Henry Miers wrote to Sir William Ramsay about

The result was characteristic; many chemists Hillebrand's observation. would have thought the observation interesting, and, when time permitted, an enquiry into the subject could be made. Not so Sir William Ramsay, who at once, on the receipt of the letter, called in the laboratory boy, and told him to go to various dealers in minerals, and bring back any cleveite that they might have. The cleveite was obtained by the middle of the day, and, before evening, it had been heated and the gas collected. During the next two days it was freed from all known gases except argon, and a residual gas was left. Confidently expecting to find argon, it was introduced into a spectrum tube. The spectrum it gave, however, was not that of argon. Instead, there appeared only a few lines; one, however, was a brilliant yellow one. It was at once suggested that it was the yellow line of sodium, due possibly to dirty electrodes, but Sir William Ramsay laughed at the idea: he was not in the habit of using dirty spectrum tubes; moreover, he had made the tube himself. At any rate, the matter could be settled at once. The light from a sodium flame was thrown into the spectroscope by means of a comparison prism, together with the light from the spectrum tube, and the two brilliant yellow lines were seen to be some distance apart in the spectrum and were not the same. It was obvious, therefore, that the gas obtained from cleveite was a new gas, and at once it was hazarded that it might be helium.

As far back as 1868, Janssen had noticed in the spectrum of the sun a brilliant yellow line that belonged to no known element. Later, Frankland and Lockyer named the element in the sun that gave this line, helium. Was this new gas of Sir William Ramsay's helium or not? The question was soon answered. The tube was sent to Sir William Crookes, who carefully measured the wave-length of the yellow line, finding it identical with the yellow solar line of helium. It had hardly taken a week, after Sir William Ramsay had received Sir Henry Miers' letter, to carry out the investigation. At the general meeting of the Chemical Society, in March, 1895, the discovery was announced of terrestrial helium in the gases evolved from cleveite when heated, and at the same meeting Lord Rayleigh was given the Faraday Medal for his discovery of argon.

During the next two years Sir William Ramsay was chiefly engaged in attempts to make helium and argon combine with other substances, but without success, also in searching for all sorts of sources from which they might be obtained. In the gases dissolved in the waters of mineral springs argon was always found to be present, and in a considerable number of rare minerals helium was found in infinitesimal quantities. This last observation was later found to be of considerable interest after it had been discovered that helium is produced by the decomposition or transmutation of radium. Meteorites and endless substances in the vegetable and animal world were also tested, but without any result. One meteorite, however, gave traces of argon and helium.

Argon and helium from their entirely negative chemical properties obviously

belonged to a group by themselves in the periodic classification of the elements by Mendeléef. At the British Association Meeting at Toronto in 1897 Sir William Ramsay, arguing from the analogy of other groups in the periodic classification, predicted the existence of at least another unknown element whose atomic weight would lie midway between argon = 39 and helium = 4, and should possess an atomic weight of about 20. The title of his paper was, "An Undiscovered Gas." To quote his words, "There should, therefore, be an undiscovered element between helium and argon, with an atomic weight 16 units higher than that of helium and 20 units lower than that of argon, namely 20, and pushing this analogy further still, it is to be expected that this element should be as indifferent to union with other elements as the two allied elements . . . . Minerals from all parts of the globe; mineral waters from Britain, France, and Iceland; meteorites from interstellar space; all these were investigated without result . . . . systematic investigation of argon, however, gave a faint indication of where to search for the missing element."

Before another year had passed his prediction had not only been verified, but, what was equally remarkable, he had in conjunction with Dr. Travers discovered two more elementary gases as well, all three belonging to the argon group. The group now contained five new gaseous elements, and this amazing result had originated in an isolated observation of Lord Rayleigh's that pure atmospheric nitrogen was slightly heavier than pure chemical nitrogen. It was a happy combination of circumstances that brought two such master workers together. It was Lord Rayleigh who by his marvellously accurate work had detected this abnormality of atmospheric nitrogen, but it was a chemist's work to solve the riddle. No chemist could have helped Lord Rayleigh better than Sir William Ramsay, but it was hard work to begin with, for they were entirely ignorant of the nature of the substance that contaminated the nitrogen.

During this work on argon and on the other four gases, nearly the whole of the apparatus used had to be invented, and much of it had to be made by Sir William Ramsay himself; in fact, the manipulation of small quantities of gas had been revolutionised and a new technique designed.

The story of the discovery of the last three gases was one of unceasing hard work, for the discovery of argon and helium had brought others into the field. It was distinctly probable, as Sir William Ramsay had pointed out at Toronto, that argon and helium were not the only members of the group. Also it was probable that they would, like argon, be found in the atmosphere, and the air is common to all. But although these others were expert scientists, they possessed neither the knowledge nor the skill for working with gases at all equal to that of Sir William Ramsay. In the end he separated Neon, Krypton, and Xenon from the air, and proved conclusively that in all probability no more inert gases were to be found in the atmosphere. It was a fit conclusion to a magnificent piece of scientific work, but it had to be done against time and with inadequate resources. With liquid air it would

have been much easier, but in the earlier parts of the research liquid air could not be obtained.

In the late autumn of 1897 Sir William Ramsay obtained his first liquid air, 100 c.c., from Dr. Hampson. By the help of this small quantity he made the discovery that there was a gas in the air heavier than argon, and that in its spectrum were two lines, one yellow and one green, that had never been noticed before. He called the gas Krypton. Later, by the help of another quantity of liquid air, he obtained from atmospheric argon a second gas lighter and more volatile than argon, that showed a large number of red and orange lines. He named it Neon, and later, after he had fractionated liquid krypton from argon, a gas heavier and less volatile than krypton was discovered in the last bubbles of gas, as the krypton evaporated. This gas was called Xenon.

To obtain these gases in a pure condition meant an incredible amount of hard work. Large quantities of atmospheric argon had been prepared with the help of Dr. Travers from air by absorbing the oxygen and nitrogen with copper and metallic magnesium, a most laborious process; finally the neon, krypton, and xenon were obtained from it in a state of purity and all their properties investigated.

Just after Sir William Ramsay had discovered krypton, he thought he had detected another element in atmospheric argon, as it had the same density as argon, but gave an entirely different spectrum; he named it Metargon, and published a preliminary account of some of the chief lines in its spectrum. Metargon did not, however, prove to be a new element, the new lines were due to traces of carbon monoxide in the argon. This was at once pointed out. The mistake was partly due to the fact that the discovery of any further new gases in the atmosphere after the discovery of argon and krypton had to be done quickly, for there were other chemists working on the same lines. To quote Sir William Ramsay: "Must one under such circumstances regret the publication of a mistake? I venture to think that an occasional error should be excused. Infallible one cannot be; and in such a state of things, one always has a large number of good friends who promptly correct the inexactitude."

Many people can make mistakes, but very few indeed could have detected krypton and xenon in the atmosphere. The first is present in the atmosphere to the amount of about 1 in 20,000,000; the second 1 in 170,000,000. Moreover, neither krypton nor xenon have ever been prepared outside Sir William Ramsay's laboratory at University College. And there only once were they separated in any quantity. With the help of Prof. Moore (now of the Bureau of Mines, U.S.A.) during 1907 and 1908, the residue from not less than 120 tons of liquid air was freed from oxygen and nitrogen, and the remaining gases thoroughly purified after separation from one another. The residue from the 120 tons had been sent to Sir William Ramsay by Monsieur Claude, of Paris. No new gases were discovered either heavier or lighter than xenon.

This work on the rare gases of the atmosphere will remain as a classical

example of scientific research. The investigation cannot be praised too highly, and an appreciation of it cannot be better expressed than in the words of Prof. Letts in 'Some Fundamental Problems in Chemistry,' p. 96: "The experimental difficulties were often profound, and they were overcome by magnificent technique. The acumen he displayed in recognising a totally new type of chemical elements was a proof of the originality of his mind, and his search for the one which, on theoretical grounds, he anticipated must exist, with its triumphant ending, show that his experimental skill and scientific acumen were, if possible, surpassed by his energy and perseverance. Can any praise be adequate in describing the work of the discoverer who detects and isolates one part of a substance in about 170 million parts of the medium in which it occurs? Yet that was exactly what Ramsay did in his discovery of xenon in the air."

It was natural that the discovery of radium by Prof. and Madame Curie, in 1902, should stimulate the fertile brain of Sir William Ramsay, and suggest all sorts of experiments with the novel substance. Dr. Soddy had come from Montreal, where he had been helping Prof. Rutherford in his work on thorium. A curious fact had been discovered, namely, that a material substance was continually being evolved from thorium. It was given the name "Emanation." Actinium and radium also gave an emanation. With all the knowledge already gained of the manipulation of small quantities of gases, Sir William Ramsay was in a favoured position for the investigation of this emanation. With Dr. Soddy he attempted to obtain the spectrum of the substance from radium, for it obviously was a gas. As the amount of emanation evolved, even from comparatively large quantities of radium bromide, is infinitesimally small, a special kind of vacuum tube had to be invented. It consisted of the finest capillary thermometer tubing with a platinum wire fused through the top, the other electrode being the mercury that could be driven up the tube with the minute quantity of emanation in front of it. They were unsuccessful in obtaining the spectrum, but were immensely surprised to find that after a spark had been passed for some time through the gas, gradually the lines of the element helium began to appear.

The magnitude of the discovery was at once apparent. It was the first instance of the transmutation of one element into another. But it was many a long day before a doubting scientific public would believe the fact. The helium had come from everywhere except the emanation, from the glass, from the mercury, from the walls of the pumps used. Almost, indeed, the most important axiom in the chemist's belief—I believe in the absolute indestructibility of the atom—was denied; the idea of the transmutation of elements had been buried centuries before with the alchemists. To soberly rehabilitate such an absurdity was the wildest nonsense. At the present day, less than fifteen years later, who doubts that radium, an element, is transmuted into the emanation, and the emanation is transmuted into helium? The walls that one generation of chemists build up so carefully

are quite ineffectual in keeping the next generation from exploring the country beyond; and, fortunately, there are the ruins of many such walls lying in the dust along the broad paths of science.

Prof. Giesel and others had shown that the energy perpetually being given out by radium and the emanation was enormous; Sir William Ramsay at once proceeded to make use of it. He argued that if sufficient radium emanation were brought into actual contact with atoms, the energy set free from the decomposing emanation might be powerful enough to shatter some of the atoms. He believed himself that he had by this treatment produced lithium from copper, and carbon from thorium and the other members of the Whether his belief was well founded or not remains thorium group. unanswered. The experiments with copper were repeated by Madame Curie, with negative results, and the thorium experiments no one has up to the present retried, for hardly anyone has sufficient radium salts to produce the amount of emanation that Sir William Ramsay used. The negative evidence of Madame Curie, however, can hardly outweigh the positive evidence of the presence of lithium. It is difficult to explain the fact that Sir William Ramsay's blank experiments where no emanation was present gave no trace

In conjunction with Dr. Whytlaw Gray, in 1910, he conducted what is perhaps the most astonishing piece of microscopical chemical work ever done. It had been shown by Rutherford and others that the emanations from thorium and radium were gases as inert as argon or the other members of the group. They probably therefore belonged to the argon group, and probably had a higher atomic weight even than xenon. Moreover, just as the solid elements of highest atomic weight, uranium, radium, and thorium, were slowly decomposing, so these elementary gases of high atomic weight were decomposing in a like manner. The only way to partly answer the question was to determine the atomic weight of the emanation from radium.

The experimental difficulties of such an investigation were enormous. Supposing even that anyone possessed 1 grm. (1000 mgrm.) of radium, it would be impossible to obtain more than 0.6 cu. mm., less than a pin's head in size, of the emanation. For it cannot be kept; in less than four days half of it has decomposed. Sir William Ramsay had no such quantity as 1 grm. of radium; the largest volume he could get of the emanation was about 0.005 cu. mm. or 0.00000032 cu. inch, an amount hardly visible. If they could determine the weight of this speck of gas, the atomic weight could be A modification of the Steele and Grant microbalance was constructed of such delicacy that a weight of Toologa mgrm. turned the scale. The details of how the infinitesimal speck of emanation was coaxed into a proper receptacle, in which it was weighed on this marvellous balance, can be found in the original paper in the 'Proceedings of the Royal Society' (vol. 84, p. 586). The mean of five determinations gave the atomic weight of 222. This fits in with a vacant space in the last or highest series of the argon group of elements in the periodic arrangement of the elements.

The name "Niton" was given to this last member of the group. Niton when pure phosphoresces, and the tint varies with the temperature of the substance. Solid niton (below  $-70^{\circ}$  C.) phosphoresces more brilliantly even than the gas. It slowly decomposes into belium and other substances, its half-life period being between three and four days. The determination of the atomic weight of niton, and the fact that it decomposed partly into helium, were facts that largely added to our knowledge of radioactive substances.

In spite, however, of the immense amount of research work produced by Sir William Ramsay, he left his mark also in many other fields of activity. As soon as he came to London he threw himself at once into all schemes that furthered the idea of a teaching university for London. He collected statistics of every kind, from the most important universities in the world, that dealt with the teaching of students and the awarding of science degrees. He wrote articles to the papers and perpetually insisted that, at least as far as the teaching of chemistry was concerned, London was far behind every other great capital.

He himself had found that, in a practical subject such as chemistry, the real life of the science lay in advance and discovery; what wonder, therefore, that he should advocate the idea that original research should play as large a part as possible, and as early as possible, in the life of a chemical student. Examinations he distrusted, that is to say, when they were the only means for testing a student, for he believed that it was often impossible to really determine the real knowledge of any student in a practical science like chemistry during a hurried few hours in an examination room, where there was no time to repair any accident, and where chance might tell either for or against the candidate. It was much more likely that the teacher, who had trained the student through three or four years, should be capable of forming a sounder judgment of the student's capacity, than anyone who merely read what that student was capable of putting down on paper under somewhat trying and limited circumstances. These ideas he always strongly advocated.

Still, after all, it is the teaching and not the result of any examination that stamps a man. Sir William Ramsay's teaching has gone out into many lands, and whether his students passed their university examinations well or badly, one thing may certainly be said, they now occupy every kind of responsible position, works managers, research chemists, analytical chemists, professors, lecturers, and teachers, and a good proportion of their success is due to the teaching and the undefinable scientific influence of Sir William Ramsay, which they absorbed whilst they were students under him.

In the technical world, he was always busy. In 1898 he was made a member of the Royal Commission on Sewage Pollution. For many years he was chairman. Endless subjects engaged his attention, from improvements in the fixation of nitrogen from the atmosphere to the composition of wax candles used in Roman Catholic churches, or to the perforation of the

pipes used to convey water to the Coolgardie Goldfields, and many other problems too numerous to mention.

In 1900 he was appointed adviser to the Indian Government on the question of university and technical education in connection with the bequest of Mr. J. N. Tata, a Parsee, of Bombay, who had left nearly half-amillion sterling to build and endow a university. Finally, Sir William Ramsay selected Bengalore as the most suitable spot. Dr. Travers, his assistant, was appointed director, and he designed and started the "Indian Institute of Science," as it was afterwards named. At this institute all sorts of technical problems and research can be prosecuted. In 1904 Sir William Ramsay visited the United States of America to attend the meeting of the International Congress of Applied Chemistry at St. Louis, where he gave an address on "Present Problems of Inorganic Chemistry." Later, in 1909, when the International Congress met in London he was President. By special request he gave a lecture to the scientific world in Berlin on the rare gases of the atmosphere, the lecture being repeated afterwards before the German Emperor. Other lectures of the same kind were given in Paris and Rome. His knowledge of foreign languages was very extensive; French and German he could speak fluently, he could also read several others as well. He was an ardent advocate of a universal language, though he himself, being so good a linguist, could hardly have felt the want. For five years he was Foreign Secretary to the Chemical Society, and in 1907 he was elected President.

Honours he had showered upon him from every country in the world. In 1895 he was given the Davy Medal of the Royal Society, in 1897 the Chemical Society awarded him the Longstaff Medal, while many foreign institutions also honoured him with medals. In 1904 he was the Nobel Laureate in Chemistry.

He was a Commander of the Crown of Italy, Officier de la Legion d'Honneur, France; Knight of the Prussian Order "Pour le Mérite"; Honorary Degrees of LL.D., D.Sc., M.D., and Ph.D., were conferred on him by numerous universities both in Great Britain and abroad. And he was made a foreign member of scientific societies in every country where they existed; Russia, Germany, Hungary, Austria, Italy, Switzerland, France, Holland, Belgium, Spain, Bohemia, Sweden, Norway, Roumania, Bengal, The United States, Mexico, and Brazil.

Looking back at the scientific work of Sir William Ramsay, the things that stand out pre-eminently are his great enthusiasm, and his marvellous capacity for investigation. For nearly 50 years he worked unceasingly, building up a worthy monument of achievement that will stand high in the annals of chemistry.

He ranged over practically the whole field of chemistry, general, inorganic, organic, theoretical, and physical, and in every section he has left his mark. A man's work is but a reflection of his mind, and Sir William Ramsay's mind was interested in every kind of chemistry and every kind of science; moreover it was a mind that always grasped big issues. He never would have been

content to make new compounds, merely because they never had been made before; if they were made it was to prove some generalisation or help on some theory of importance. Hence nearly all his researches had reference to useful and often fundamental ideas in chemistry. Being an unrivalled experimentalist, possessing a capacity for work given to few, he was able to explore the unknown in a manner impossible to less skilled workers, and, as all that he did was guided by a far-seeing and intensely enthusiastic mind, it is no wonder that he advanced the science of chemistry in a manner that will be valued very highly by posterity.

Every novel scientific fact or idea interested him at once, and acted as a stimulus for further work. No new problem ever appeared to him too difficult; with a perfect fearlessness and total disregard of all difficulties, he would rush into new fields and gather a return for his courage, whilst the more cautious were wondering whether they might venture into so unknown, and probably so dangerous, a country. Sir William Ramsay it was who first taught in England the new ideas on the theory of solutions of Arrhenius and Van't Hoff. He it was who first demonstrated by experiment one evening to the Chemical Society that the moleular weight of compounds could be determined by the lowering of the freezing point of the solvent, and the audience were sadly sceptical. Sir William Ramsay was the first to try the action of the emanation of radium on cancer patients. He was always a pioneer.

His spirit of enthusiasm and research he has handed on to the younger generation who worked with him. The good a man does lives after him, and no British chemist has sown the seed of the true gospel of scientific discovery with a more lavish hand than Sir William Ramsay.

His fame as a chemist will rest chiefly on his discoveries. Great discoveries, once they are made, often seem so simple. But the world does not know of the toil spent on unproductive results, before the final discovery emerges, and of the years of hard work that are necessary to make a man a master of his craft. It was the years of hard work from 1870 to 1887, before Sir William Ramsay came to London, that enabled him to discover the rare gases. For during that time he had learnt his trade, and was able to use all the resources of a laboratory, and, more than that, he was able to supplement those resources by inventions of his own when occasion required. The whole art of working with small quantities of gases, the Ramsay burner, constant-temperature jackets, are some of the practical legacies he has left the chemist.

It is only natural, being such a wonderful experimentalist, that he never was more happy than when he was in his laboratory. There he would work, making his own apparatus, bending to his purpose every kind of material, great and small, for he could use them all with a master's hand, and produce marvels. But to be a master worker is only a means to an end, there must also be the master mind, a mind that, without neglecting small things, sees great ones beyond and pursues them. Such a mind had Sir William Ramsay.

With his great imagination, great vitality, great persistence, he saw far down the corridors of time, new vistas allured him ever onward, the small things by the roadside interested him, but his gaze ever was fixed on the far off hills and on the great mountains of the far distant and unknown country beyond. Some of that unknown country he was happy enough to win to but some he only saw lit up by the dawn, and—

"This high man, with great things to pursue,
Dies ere he knows it."

J. N. C.

### WILLIAM ESSON (1839—1916).

WILLIAM ESSON was born on May 17, 1839, at Carnoustie, in Forfarshire.\* But the entry in the Oxford Register of Matriculations of date March 8, 1855, runs "Coll. D. Jo. Bapt., Esson Gulielmus, XVI, in opp. Dundee in Scotia, Gulielmi Gen. fil. unicus," and an old friend, with whom he exchanged yearly congratulations (in Greek verse) as with one of the same age to a day, gives the date May 17, 1838. His father, Mr. William Esson, was a talented gas engineer who moved with his family from Carnoustie to Inverness in 1843, and from Inverness came south to Cheltenham in 1853. Hence it befell that William's school training, received in the main at the Inverness Royal Academy, was completed by not more than two years of instruction under the well-known mathematician H. M. Jeffery at Cheltenham Grammar School. At Inverness he showed himself a young boy of remarkable and varied gifts, obtaining the Gold Medal for Mathematics in 1852, and that for Latin and Greek a year later. At Cheltenham Jeffery found in him a pupil after his own heart, and one can well imagine that his pride at the boy's success was mingled with pain at early separation from him when, as the story at St. John's College, Oxford, runs, he talked of the lad's promise so enthusiastically on the occasion of a visit to the College early in 1855, that-having then no open scholarships—it secured him without delay as Bible Clerk.

Notwithstanding extreme youth, Esson proceeded to carry all before him in Mathematics, and to show himself no forced specialist by successes in other fields. By the end of 1856, i.e., at 17½ if the later of the dates given for his birth is correct, he had gained a First Class in Mathematical, and a Second in Classical Moderations. In brisk succession followed the University Junior Mathematical Scholarship, a Second in the Final Classical School, a First in the Final Mathematical, and the Senior Mathematical Scholarship. To

<sup>\*</sup> This definite statement comes from a family source.

achieve all this while yet a mere boy required a sound body as well as a strong mind; and for the next 50 years, his magnificent beard having grown, Esson's aspect proclaimed to all Oxford the health and force that were in him.

He was elected Fellow of Merton in 1860, and appointed Mathematical Lecturer and Tutor of the College in 1865. Four other Colleges—Magdalen, Corpus, Worcester, and Hertford—entrusted their mathematical students to him as Tutor or Lecturer for extended periods. His pupils were well off, and enthusiastic as to their advantages.

No name is more closely associated than Esson's—perhaps none equally closely—with the initiation of three great reforms in Oxford, which have been consummated during his academical life. In two of them he was a prime mover, and in the third an earliest beneficiary.

Take first the last mentioned—the profound change in the social conditions of senior Oxford, which had not begun when he was elected at Merton, but was just about complete when the dispersal of 1914 came. In 1872 his College obtained a new Statute, the first of its kind, which authorised four of its staff to marry without vacating their Fellowships. Esson was one of the four; and he exercised the new right on July 10, 1872. Mrs. Esson, a charming woman, was Eliza, daughter of the Rev. James Meek, of the Manse, Carnoustie. She only lived till November 11, 1893. They had two sons and a daughter. The latter, Mrs. Edmund Gay, survives her father. Of the sons one, James, died in his 21st year, and the other, William, Major R.M.L.I., went down with H.M.S. Russell last year. The final failure of the father's health at once began, and he passed away on August 25, 1916.

The other two reforms referred to were in matters of college teaching, one concerned with the well-being of individual students, and one with the organisation of co-operative effort in the provision of lectures. First came the destruction in Oxford—things did not move quite so fast at Cambridge of the unworthy tradition that in order to obtain the highest honours an undergraduate must pay large sums to a private tutor. Esson, and a few with him, quietly set to work giving to college pupils as individuals all the personal attention which their circumstances at the moment required. Success crowned their efforts; emulation set in among tutors other than mathematical, and a revolution was effected. How Esson managed to make the most of us-I write as a grateful pupil-I have always found it hard to say. He talked little, wrote little, praised little, blamed little; but somehow when, after sitting before a large sheet of paper with him for half an hour, one had come away digesting a nutshellful of essential ideas, and bearing a comparatively small corner of the sheet with some jottings on it, the difficulties which had seemed insurmountable were found to have vanished. Years later, when it became our turn to take the other chair before the sheet of paper, we could not manage the trick as he had done, but had to adopt system with a danger of dullness, or perhaps to ease our minds by working hard for pupils with lack of skill in the more important aim of inducing them to work hard for themselves. But there was no return to the pernicious easy-going attitude of advisers on whom little responsibility rested.

The remaining new departure, for which no small share of the credit should be assigned to Esson, was the institution more than fifty years ago of the system of Inter-Collegiate Lectures. The Mathematical Association of College Lecturers (not of colleges) was at any rate one of the first-was, I believe, the very first-of such combinations. Whether the idea of it originated with Esson himself or with Henry Smith (who was Tutor of Balliol as well as Savilian Professor) I do not know, but the then young generation certainly looked on Esson as the soul of it. His lectures drew large and willing classes, being both eminently practical for examination purposes and stimulating to men of capacity. The rank and file could not accuse him of talking over their heads, nor the few complain "It is all in the books." His expression was studiedly crisp, and he already showed the taste for clipped nomenclature, which later on he indulged, as some thought, The combination system has long since developed into one made universal under Faculty Statutes adopted by, and imposed upon, the University; but reforming zeal gravitates into conservatism, and only last year did the Oxford mathematicians apply to be recognised as a sub-faculty rather than remain a professedly voluntary co-optative association.

When, in 1894, Prof. Sylvester found he could no longer discharge the duties of his Savilian Professorship of Geometry, Esson was appointed Deputy Professor, with universal approval. He had not—nor had anyone else available—made himself widely known by authorship as a learned geometrical specialist—indeed, his best published work had been markedly non-geometrical. But Oxford knew him well, not only as undisputed leader among those teachers who had raised its mathematical schools to a level of which it was proud, but also as pre-eminent among lecturers on geometry. Three years later Sylvester died, and Esson succeeded to the Chair.

Both regret and surprise have been felt that, being a geometer, he wrote so little on geometry. A few elegant notes on analytical methods in his young days, and two highly condensed papers on the "Characters of Plane Curves" in his late life, were, I think, all. The late papers were no doubt extracted from material which he has been understood to be amassing, for many years past, in preparation for a work on 'Higher Plane Curves.' This has not been left in a state for publication, though parts have been written and re-written.

Happily the initiative of another early led him to work in a different field which bore rich fruit. As a young man, he found some time for experimental chemistry, and came under Mr. (now Dr.) A. G. Vernon Harcourt as Chemical Demonstrator. Harcourt began a research on the conditions of chemical change, and invited Esson to join him in the investigation. Shoulder to shoulder they worked together for years, Harcourt planning the experiments, both attending to every detail and checking one another's observation of time intervals, Esson doing the calculations. These estab-

lished to the hilt the accuracy of the law that, in unit volume of a dilute solution at constant temperature, the rate of chemical change varies directly with the mass of each of the interacting substances. It was pioneer work, and secured sure, if not speedy, recognition as novel and general in character, flawless in execution, and mathematically sound. Its method prevails till this day. The record of it is to be found in the 'Philosophical Transactions' for 1864 and 1866. Many years later the two resumed the work. The Bakerian Lecture of 1905 is a joint production as before. A later paper ('Phil. Trans.,' 1912) is entirely Harcourt's as a record of experiment, but is accompanied by an Appendix, which is entirely Esson's. The law of the rate k of a chemical action under known conditions at one temperature having been completely established, a problem of the Bakerian Lecture, and the main one of the latest paper in the series, is to estimate changes of k as the temperature changes. Esson proves that the law of connection

$$\frac{k}{k_0} = \left(\frac{t+c}{t_0+c}\right)^m$$

is satisfied in all Harcourt's experiments, with c = 272.6, and m one positive constant or another. In the Appendix the same law is found to agree with many experimental results obtained by other chemists under circumstances free from disturbing conditions. Esson proceeds boldly to propound the same law, but with m dependent on the temperature, as applicable under all circumstances, and examines the ranges of m for certain ranges of t in a few researches where the hypothesis m constant fails. He does not get so far as to indicate laws determining m as a function, and it cannot be said that his generalisation has yet secured acceptance. But, even without this, the ungeneralised law for simple actions goes far in justification of the statement that, at the zero of absolute temperature, not only do gases exert no pressure, their molecules having ceased to move, but atoms also cease to move, so that, in Harcourt's words, "iodine and potassium will lie down together." For Esson's last word on laws of which the above is one, a note in the 'Proceedings of the Fifth International Congress of Mathematicians,' Cambridge, 1912 (vol. 2, p. 272), may be consulted.

He was elected a Fellow of the Royal Society in 1869, and was also F.C.S., F.R.A.S., and for just 50 years a member of the London Mathematical Society. He was a member of the Alpine Club.

In Oxford he was Chairman of the Board of the Faculty of Natural Science for 15 years, ending in 1913, a Visitor (and Secretary to the Visitors) of the University Observatory, a Delegate of Local Examinations, a Delegate of the Common University Fund, and a Curator of the Chest, all for very long periods. His services as financier and man of business to the University and to Merton College, of which he remained Bursar even after he became Fellow of New College as Professor, were unremitting and very highly valued.

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